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Some Thermodynamic Properties
of Water
and Aqueous Electrolytes



Lund 1979



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The enthalpy of ionization of water between 273 and 418 K has been determined calorimetrically. The results are used to evaluate an equation of ΔC_p^0 as a function of temperature, leading to equations for the temperature dependence of ΔH_i^0 and K_w^0 . Heat capacity measurements on NaCl, KCl, and KNO_3 solutions up to 3 mol kg⁻¹ have been made with one LKB reaction-solution calorimeter and two Picker flow microcalorimeters to check the accuracy of the flow calorimetric measurements. Apparent molar heat capacities and apparent molar volumes, at constant pressure and 298.15 K, have been determined for 28 aqueous electrolytes of charge types 1:1, 2:1, 3:1, and 4:1.

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Apparent molar heat capacities and volumes of aqueous NaCl, KCl, and KNO₃ at 298.15 K. Comparison of Picker flow calorimeter with other calorimeters

INGER V. OLOFSSON ^a

Department of Chemistry, University of Lethbridge,
Lethbridge, Alberta Canada T1K 3M4

^a On leave from Thermochemistry Laboratory, Chemical Center,
University of Lund, S-220 07 Lund, Sweden

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Send proofs to: Inger Olofsson, Thermochemistry Laboratory, Chemical
Center, P.O.B. 740, S-220 07 Lund, Sweden

Abstract

Measurements have been made at constant pressure and 298.15 K, leading to apparent molar heat capacities and apparent molar volumes, of aqueous NaCl, KCl, and KNO₃. Heat capacities of solutions up to 3 mol kg⁻¹ have been determined with one LKB reaction-solution calorimeter and two Picker flow calorimeters. The results are used, together with those reported in the literature, to analyze the accuracy of the Picker flow calorimeter.

For aqueous NaCl a recommended best value of the partial molar heat capacity at infinite dilution, $C_{p,\phi}^{\circ} = -84.3 \text{ J K}^{-1} \text{ mol}^{-1}$, is chosen.

1. Introduction

Flow microcalorimetry^(1,2) has proven to be very useful for the determination of heat capacities of aqueous electrolyte and nonelectrolyte solutions. Heat capacities can be determined with high precision, but the accuracy is still uncertain. Desnoyers et al.⁽³⁾ have discussed the accuracy of flow microcalorimeters and sources of systematic errors. They pointed out the need for a chemical standard and recommended NaCl to be used for aqueous electrolyte solutions.

Results from earlier investigations on solutions of NaCl, KCl, and KNO₃, have been critically examined. As there are questions about accuracy of data on dilute solutions determined with other types of calorimeters, we have focussed on results from measurements on concentrated solutions. Heat capacity data, reported in the literature together with the results from our measurements, have been used to compare the Picker flow calorimeter with other calorimeters. These comparisons have been used to correct results from measurements with Picker flow calorimeters on dilute solutions.

2. Experimental

Heat capacity measurements on concentrated solutions were made with an LKB-8700 reaction-solution calorimeter using a glass reaction vessel. The vessel was filled with 105.0 cm³ calorimeter liquid and was weighed to 0.01 g. Vessel plus content was heated electrically 300 seconds, using the 500 mW power range. The corresponding decrease in the resistance of the thermistor was determined by graphical extrapolation based on Dickinson's method. The thermistor used was calibrated at 298.03 and 303.03 K by comparison against a calibrated quartz thermometer. The resistance of the thermistor was converted to temperature using the relation:

$$\ln R = A + \frac{B}{T} \quad (1)$$

The LKB reaction-solution calorimeter has also been used earlier to determine heat capacities of NaCl solutions.⁽⁴⁾ The experiments were carried out in a way similar to that described here.

Heat capacities were also measured with two Picker flow calorimeters. The measurements on dilute solutions were made relative to water. Solutions more concentrated than 0.25 mol kg^{-1} were measured relative to more dilute solutions, with some measurements made relative to water as well.

Densities of all solutions used with the flow calorimeter have been measured as described previously.⁽⁵⁾ The density of water has been taken as $0.997047 \text{ g cm}^{-3}$.⁽⁶⁾

Results of all measurements refer to 298.15 K.

Solutions were prepared from dried samples of salts and boiled, double distilled water by mass. Fisher certified KCl was ground and dried at 473 K, Fisher certified KNO_3 was ground and dried at 378 K, and BDH analar NaCl was ground and dried at 823 K. All dried samples were stored in desiccators over silica gel.

3. Results

MEASUREMENTS WITH THE LKB CALORIMETER

A series of calibration experiments were made, when the vessel was filled with 105.0 cm^3 water weighed to 0.01 g. Calibration energy of 150.54 J was used. By subtracting the contribution of the water from the total heat capacity of the system, the heat capacity of the vessel was determined. The mean values and the estimated standard deviations s_m of the means are given in addition to the results of the individual experiments in table 1. When

the vessel was connected with a closer fitting to the lid the heat capacity of the vessel became slightly larger, as is the case in the second set of data.

The results of the calorimetric measurements on NaCl, KCl, and KNO₃ solutions are summarized in table 2. We have assumed that the heat capacity of the vessel is the same, when the vessel is filled with saline solutions of various concentrations, as when it is filled with the same volume pure water.

The apparent molar heat capacities of solutes were calculated from measured heat capacities by way of the equation

$$C_{P,\phi} = c_P M_2 + \frac{(c_P - c_P^O)1000}{m} \quad (2)$$

in which the symbols have the following meanings: $C_{P,\phi}$ is the apparent molar heat capacity of solute expressed in terms of $J K^{-1} mol^{-1}$, c_P and c_P^O are the heat capacities of solution and of pure water expressed in terms of $J K^{-1} g^{-1}$, M_2 is the molecular weight of solute, and m is the molality of solution expressed in terms of (moles of solute) $(kg H_2O)^{-1}$. In all calculations $c_P^O = 4.1793 J K^{-1} g^{-1}$ has been used. (7)

MEASUREMENTS WITH THE FLOW MICROCALORIMETER

Results of flow calorimetric measurements are heat capacities per unit volume of solution. Combination of these heat capacities with the densities that we have also measured and the already known heat capacity of water permits calculations of heat capacities of solutions expressed in terms of $J K^{-1} (g \text{ solution})^{-1}$. These heat capacities of solutions are used to calculate the apparent molar heat capacities of solutes using equation (2). Similarly densities of solutions lead to the apparent molar volumes of solutes using the equation:

$$V_{\phi} = \frac{M_2}{d} + \left(\frac{1}{d} - \frac{1}{d_1^0}\right) \frac{1000}{m} \quad (3)$$

in which the symbols have the following meanings: V_{ϕ} is the apparent molar volume of solute expressed in terms of $\text{cm}^3 \text{mol}^{-1}$, d and d_1^0 are the densities of solution and of water expressed in terms of g cm^{-3} , M_2 is the molecular weight of solute, and m is the molality of solution expressed in terms of $(\text{moles solute}) (\text{kg H}_2\text{O})^{-1}$. $d_1^0 = 0.997047 \text{ g cm}^{-3}$ has been used. ⁽⁶⁾

Results of measurements made in 1977 with a Picker flow calorimeter have been used to calculate the apparent molar heat capacities that are listed in table 3. The corresponding apparent molar volumes are given there also. The apparent molar heat capacities that are listed in table 4 refer to measurements made in 1978 with a new Picker flow calorimeter.

For dilute solutions of strong electrolytes the apparent molar properties are accurately represented by equations of the form

$$Y_{\phi} = Y_{\phi}^0 + A_y (d_1^0 m)^{1/2} + B_y m \quad (4)$$

in which Y_{ϕ}^0 is the value of Y_{ϕ} at infinite dilution, A_y is the limiting slope derived from the Debye-Hückel theory, m is the molality, and B_y is an adjustable parameter. Measurements on dilute solutions have been made in order to determine the $C_{p,\phi}^0$ and V_{ϕ}^0 values that are identical with the corresponding partial molar properties at infinite dilution, $\bar{C}_p^0$ and $\bar{V}^0$. For these calculations we have used $A_c (d_1^0)^{1/2} = 28.95 \text{ J K}^{-1} \text{mol}^{-3/2} \text{kg}^{1/2}$ and $A_v (d_1^0)^{1/2} = 1.865 \text{ cm}^3 \text{mol}^{-3/2} \text{kg}^{1/2}$. The $C_{p,\phi}^0$, B_c , V_{ϕ}^0 and B_v values given in table 5 are based on least squares fitting the results from tables 3 and 4 for molalities less than 0.50 mol kg^{-1} to equations of type (4) with the limiting slopes specified above. The standard errors of estimate σ in $C_{p,\phi}^0$ and V_{ϕ} are also given where

$$\sigma^2 = \frac{\sum [\bar{Y}_\phi - \bar{Y}_\phi(\text{calc})]^2}{n-2}$$

COMPARISONS

Desnoyers et al.⁽³⁾ have investigated the accuracy of their Picker flow calorimeter and defined a correction factor due to heat leak between the heating element in the calorimeter and the calorimeter jacket. The factor f is the ratio of the true change in heat capacity per unit volume from reference liquid to solution to the calorimetrically obtained one, which can be expressed as

$$f = (\Delta c'_p / c'_{p,1}) / (\Delta c'^*_p / c'_{p,1}) \quad (5)$$

where $c'_{p,1}$ is the heat capacity per unit volume of reference liquid, $\Delta c'_p$ is the true difference between the heat capacities per unit volume of solution and of reference liquid, and $\Delta c'^*_p$ is the uncorrected calorimetrically obtained difference in the heat capacities per unit volume.

Heat capacities of NaCl solutions reported by earlier investigators have been critically examined. Good agreement is found between values reported by Randall and Rossini,⁽⁸⁾ by Hess and Gramke,⁽⁹⁾ and by Tanner and Lamb⁽¹⁰⁾ for solutions that are more concentrated than 0.5 mol kg⁻¹. Their results together with results from measurements with our LKB calorimeter reported in this work have been taken to give the best set of data of apparent molar heat capacities of aqueous NaCl in the concentration range 0.5 mol kg⁻¹ to 3.2 mol kg⁻¹ at 298.15 K. By unweighted least squares fit of $C_{p,\phi} - A_c (d_1^0 m)^{1/2}$ versus molality, the following second order polynomial was found to represent the data;

$$C_{p,\phi} - A_c (d_1^0 m)^{1/2} = a_0 + a_1 m + a_2 m^2 \quad (6)$$

where $A_c (d_1^o)^{1/2} = 28.95 \text{ J K}^{-1} \text{ mol}^{-3/2} \text{ kg}^{1/2}$, $a_0 = -85.19 \text{ J K}^{-1} \text{ mol}^{-1}$, $a_1 = 18.22 \text{ J K}^{-1} \text{ mol}^{-2} \text{ kg}$, and $a_2 = -1.827 \text{ J K}^{-1} \text{ mol}^{-3} \text{ kg}^2$. The standard error of estimate in $C_{p,\phi} - A_c (d_1^o)^{1/2}$ was $0.42 \text{ J K}^{-1} \text{ mol}^{-1}$.

Measurements on concentrated NaCl solutions with flow microcalorimeter have been reported by Picker et al.⁽¹⁾ and by Fortier et al.⁽¹¹⁾ We have used their results together with the results from our measurements with two different flow calorimeters and calculated the correction factor f , for each calorimeter and each concentration, using the relation:

$$f = \frac{C_{p,\phi} - V_\phi c'_{p,1}}{C_{p,\phi}^* - V_\phi c'_{p,1}} \quad (7)$$

where $C_{p,\phi}$ is the "true" apparent molar heat capacity at each concentration at which flow calorimetric measurements have been carried out. $C_{p,\phi}$ is calculated from the least squares fit of $C_{p,\phi} - A_c (d_1^o)^{1/2}$ mentioned above. $C_{p,\phi}^*$ is the uncorrected apparent molar heat capacity determined with flow calorimeter, V_ϕ is the apparent molar volume, and $c'_{p,1}$ is the volumetric heat capacity of water. $c'_{p,1} = 4.1670 \text{ J K}^{-1} \text{ cm}^{-3}$ has been used. The results are shown in figure 1.

For concentrated KCl solutions there is not such a good agreement between heat capacities reported in the literature. We have used results reported by Tanner and Lamb⁽¹⁰⁾ together with our results with our LKB calorimeter and evaluated "true" $C_{p,\phi}$ graphically at each concentration of interest. Fortier et al.⁽¹¹⁾ have made measurements on KCl solutions with flow calorimeter. We have used their results and results from our measurements on flow calorimeter and calculated a correction factor for each calorimeter at each concentration. The results are shown in figure 2.

For concentrated solutions of KNO_3 we have taken the apparent molar heat capacities from our measurements with LKB to be "true". Our results

from measurements on solutions more concentrated than 0.5 mol kg^{-1} with flow calorimeter have been least squares fitted as $C_{p,\phi} - A_c(d_m^O)^{1/2}$. Flow calorimetrically obtained apparent molar heat capacities have been calculated at each concentration at which LKB measurements have been carried out and the calculated f values are shown in figure 2.

These calculated f values have been used to correct flow calorimetric data on dilute solutions. The corrected apparent molar heat capacities have been calculated by use of the relation

$$C_{p,\phi} = C_{p,\phi}^* \cdot f + (1-f)V_\phi c'_{p,1} \quad (8)$$

in which the symbols have the same meanings as above.

In these calculations we have used individual f values for each calorimeter and each salt. As is indicated in the figures we have taken f to be dependent on concentration for the two calorimeters used in this work. There is no such indication from results reported by Picker et al.⁽¹⁾ and by Fortier et al.⁽¹⁰⁾ and we have used an average f for each salt for those two calorimeters.

Corrected apparent molar heat capacities for molalities 0.05 to 0.50 mol kg^{-1} have been fitted by least squares to equations of type (4) as described above. The corrected $C_{p,\phi}^O$ and B_c values, with corresponding standard errors of estimate, from our calculations plus results reported by other investigators⁽¹⁰⁻¹⁶⁾ are listed in table 6. The correction factors f which have been used to correct the apparent molar heat capacities are listed there also. For the results from the flow calorimetric measurements mean values of corrected $C_{p,\phi}$ and B_c are given for each salt.

The partial molar volumes of aqueous KCl, NaCl, and KNO_3 determined in this investigation are all in good agreement with corresponding values chosen by Millero⁽¹⁷⁾ as the "best" values.

4. Discussion

Heat capacity measurements on aqueous NaCl seem to be very reproducible and we support the recommendation by Desnoyers et al.⁽³⁾ for NaCl to be used as a chemical standard in flow calorimetric measurements on aqueous electrolytes. The best value of partial molar heat capacity of aqueous NaCl seems to be $C_{p,\phi}^0 = -84.3 \text{ J K}^{-1} \text{ mol}^{-1}$ with a standard deviation $0.7 \text{ J K}^{-1} \text{ mol}^{-1}$ and the best adjustable parameter $B_c = 14.6 \text{ J K}^{-1} \text{ mol}^{-2} \text{ kg}$ with a standard deviation $1.4 \text{ J K}^{-1} \text{ mol}^{-2} \text{ kg}$.

For the flow calorimeter we used in 1977 the comparisons with other calorimeters lead to corrections in partial molar heat capacities of -3.0 and $-2.9 \text{ J K}^{-1} \text{ mol}^{-1}$ for NaCl and KCl, respectively. Even though these corrections are larger than expected they are within the uncertainty limits $\pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$ earlier claimed for this calorimeter.

For the flow calorimeter we used in 1978 the corresponding corrections became $-6.2 \text{ J K}^{-1} \text{ mol}^{-1}$ for both NaCl and KNO_3 .

There are some problems connected with using a correction factor f , defined by Desnoyers et al.⁽³⁾ as there are indications that f can vary from one calorimeter to another and seems to be slightly dependent on electrolyte and concentration. Further investigations are needed to make clear how to best indicate and correct for these small systematic errors in flow micro calorimeters.

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TABLE 1. Heat capacity of the LKB glass reaction vessel at 298.15 K

<u>amount</u> g	<u>c_p</u> (vessel) J K ⁻¹
104.73	20.73
104.72	20.80
104.71	20.50
104.76	20.66
104.72	20.46
104.72	20.74
104.75	20.35
104.75	20.61
104.71	20.67
104.71	20.69
mean = 20.62	
s _m = 0.04	
104.64	20.81
104.64	20.99
104.52	20.98
104.52	21.14
104.74	20.85
104.74	20.87
104.62	20.57
104.56	20.91
mean = 20.89	
s _m = 0.06	

TABLE 2. Apparent molar heat capacities at constant pressure and 298.15 K,
determined with an LKB reaction calorimeter. $c_p(\text{vessel}) = 20.62 \text{ J K}^{-1}$
unless otherwise stated.

m mol kg^{-1}	amount g	c_p $\text{J K}^{-1} \text{ g}^{-1}$	$C_{p,\phi}$ $\text{J K}^{-1} \text{ mol}^{-1}$
KCl			
0.9942	109.41	3.8166	-78.37
1.4887	111.45	3.6706	-68.07
2.1060	114.07	3.5079	-57.28
NaCl			
1.0203	112.70	3.9075	-38.12 ^a
1.0203	112.70	3.9074	-38.19 ^a
1.4193	110.44	3.8209	-29.25
1.4193	110.44	3.8226	-27.94
2.0154	112.57	3.7107	-15.66
2.0154	112.57	3.7116	-15.20
2.5416	114.55	3.6283	- 4.75
2.5416	114.59	3.6273	- 5.23
2.5416	114.59	3.6281	- 4.84
2.7982	115.21	3.5901	- 0.77 ^c
2.7982	115.21	3.5900	- 0.80 ^c
3.1947	118.24	3.5390	+ 6.39 ^b
3.1947	118.24	3.5391	+ 6.41 ^b

Cont.

TABLE 2. Cont.

$\frac{m}{\text{mol kg}^{-1}}$	$\frac{\text{amount}}{g}$	$\frac{c_p}{\text{J K}^{-1} g^{-1}}$	$\frac{c_{p,\phi}}{\text{J K}^{-1} \text{mol}^{-1}}$
KNO_3			
1.9098	115.88	3.5567	33.59
1.9098	115.88	3.5579	34.34
1.9816	116.35	3.5398	35.14
1.9816	116.35	3.5386	34.41
2.4302	118.41	3.4395	43.30 ^c
2.4302	118.41	3.4404	43.81 ^c
2.9235	120.94	3.3407	50.90 ^c
2.9235	120.94	3.3404	50.79 ^c

^a Reference 4, $c_p(\text{vessel}) = 14.39 \text{ J K}^{-1}$

^b Reference 4, $c_p(\text{vessel}) = 14.22 \text{ J K}^{-1}$

^c $c_p(\text{vessel}) = 20.89 \text{ J K}^{-1}$

TABLE 3. Apparent molar heat capacities (constant pressure) and volumes at 298.15 K. Heat capacities determined with a Picker flow calorimeter in 1977

m	$C_{p,\phi}$	V_ϕ	m	$C_{p,\phi}$	V_ϕ
mol kg ⁻¹	J K ⁻¹ mol ⁻¹	cm ³ mol ⁻¹	mol kg ⁻¹	J K ⁻¹ mol ⁻¹	cm ³ mol ⁻¹
KCl			NaCl		
0.04642	-106.2	27.69	0.06333	-73.4	17.33
0.08221	-105.0	27.68	0.07845	-72.2	17.32
0.11238	-103.5	27.79	0.07977	-71.9	17.66
0.14839	-100.5	27.84	0.08133	-72.1	17.27
0.17219	-99.7	27.86	0.10101	-70.5	17.40
0.20274	-97.7	27.94	0.10167	-71.3	17.40
0.29381	-96.2	28.10	0.14945	-67.6	17.72
0.36860	-93.2	28.17	0.21141	-65.5	17.50
0.48243	-89.7	28.38	0.21276	-65.3	17.48
0.5687	-87.0	28.44	0.42262	-56.9	17.84
0.6066	-86.0	28.54	0.46038	-55.2	17.89
0.7618	-81.6	28.69	0.46770	-54.6	17.90
0.8096	-80.7	28.76	0.6687	-48.0	18.18
0.9414	-77.1	28.89	0.7722	-44.4	18.26
1.0096	-76.1	28.95	0.7770	-44.2	18.30
1.1593	-72.5	29.09	0.9127	-40.4	18.44
1.2157	-71.7	29.14	1.1658	-33.0	18.67
1.4195	-67.4	29.36	1.1947	-32.3	18.70
1.6048	-64.2	29.49	1.3869	-27.6	18.88
1.8470	-59.8	29.71	1.6077	-22.1	19.05
2.0087	-57.3	29.81	2.0987	-11.6	19.42

TABLE 4. Apparent molar heat capacities (constant pressure) and volumes at 298.15 K. Heat capacities determined with a new Picker flow calorimeter in 1978.

m	$C_{P,\phi}$	V_ϕ	m	$C_{P,\phi}$	V_ϕ
mol kg ⁻¹	J K ⁻¹ mol ⁻¹	cm ³ mol ⁻¹	mol kg ⁻¹	J K ⁻¹ mol ⁻¹	cm ³ mol ⁻¹
KNO ₃			NaCl		
0.06145	-43.1	38.41	0.06662	-68.9	16.79
0.06959	-42.2	38.94	0.07699	-68.4	16.91
0.07455	-42.1	38.77	0.08004	-68.7	16.95
0.08660	-39.3	38.97	0.09945	-67.2	17.04
0.10443	-38.6	38.96	0.11976	-65.4	17.13
0.12041	-37.1	39.01	0.14167	-64.9	17.19
0.14066	-34.9	39.07	0.17690	-63.5	17.25
0.16696	-33.4	39.12	0.17842	-63.3	17.26
0.19737	-30.6	39.16	0.19749	-62.4	17.35
0.24078	-27.6	39.25	0.42086	-52.8	17.74
0.33905	-19.1	39.46	0.6504	-44.3	18.10
0.5593	-7.8	39.82	0.6520	-45.8	18.10
0.7017	-0.7	40.01	0.9208	-37.8	18.33
0.9059	+7.9	40.22	1.1888	-30.7	18.55
0.9864	+10.4	40.31	1.5088	-22.4	18.90
1.1649	+17.1	40.56	1.9384	-13.5	19.24
1.2361	+19.8	40.59	2.0889	-10.5	19.36
1.2480	+19.5	40.64	2.3666	-5.1	19.57
1.5869	+28.7	40.92	2.8116	+2.4	19.83
1.6803	+32.3	40.99			
2.0732	+39.6	41.32			
2.4653	+46.4	41.56			

TABLE 5. Parameters for equation $Y_\phi = Y_\phi^0 + A_y (d_1^0 m)^{1/2} + B_y m$. Concentrations less than 0.50 mol kg^{-1} used.

Solute	$C_{P,\phi}^0$ J K ⁻¹ mol ⁻¹	B_c J K ⁻¹ mol ⁻² kg	V_ϕ^0 cm ³ mol ⁻¹	B_V cm ³ mol ⁻² kg
KCl	-113.2 $\sigma = 0.7$	6.7	27.29 $\sigma = 0.04$	-1.09
NaCl	-81.5 $\sigma = 0.3$	14.5	17.19 $\sigma = 0.12$	-1.95
KNO ₃	-53.2 ^a $\sigma = 0.5$	49.8 ^a	38.41 $\sigma = 0.06$	-0.39
NaCl	-77.6 ^a $\sigma = 0.4$	13.6 ^a	16.32 $\sigma = 0.04$	+1.03

^a Measurements made in 1978 with a new flow calorimeter

TABLE 6. Parameters for equation $C_{P,\phi} = C_{P,\phi}^0 + A_c (d_1^0 m)^{1/2} + E_c m$.
 Results from flow calorimetric measurements are corrected as follows by f .

Investigator	f	$C_{P,\phi}$ $J\ K^{-1}\ mol^{-1}$	s	E_c $J\ K^{-1}\ mol^{-2}\ kg$	s
NaCl					
Parker ⁽¹²⁾	-	-90 ^c			
Criss and Cobble ⁽¹³⁾	-	-79.1 ^c			
Tanner and Lamb ⁽¹⁰⁾	-	-85.1 ^c	1.4	6	14
Picker et al. ⁽¹⁾	1.012	-85.4	0.7	14.8	1.6
Fortier et al. ⁽¹¹⁾	1.021	-83.5	0.6	12.3	1.7
Singh et al. ⁽¹⁴⁾	1.020	-84.6	0.4	13.4	1.3
Allred and Woolley ⁽¹⁵⁾	1.000	-84.1	0.7	15.7	1.4
This work ^a	1.020	-84.5	0.3	15.3	0.8
This work ^b	1.043	-83.8	0.4	16.0	1.3
		mean = -84.3		mean = 14.6	
		s = 0.7		s = 1.4	
KCl					
Parker ⁽¹²⁾	-	-114.6 ^c			
Tanner and Lamb ⁽¹⁰⁾	-	-117.1 ^c			
Fortier et al. ⁽¹¹⁾	1.027	-115.8	1.0	7.0	2.5
This work ^a	1.013	-116.1	0.7	7.2	1.8
		mean = -116.0		mean = 7.1	
KNO ₃					
Parker ⁽¹²⁾	-	-64.8 ^c			
Enea et al. ⁽¹⁶⁾	1.000	-59.8	0.4	49.9	1.7
This work ^b	1.030	-59.4	0.5	51.9	1.8
		mean = -59.6		mean = 50.9	

^a Measurements made in 1977. ^b Measurements made in 1978. ^c Not used when calculating mean values.

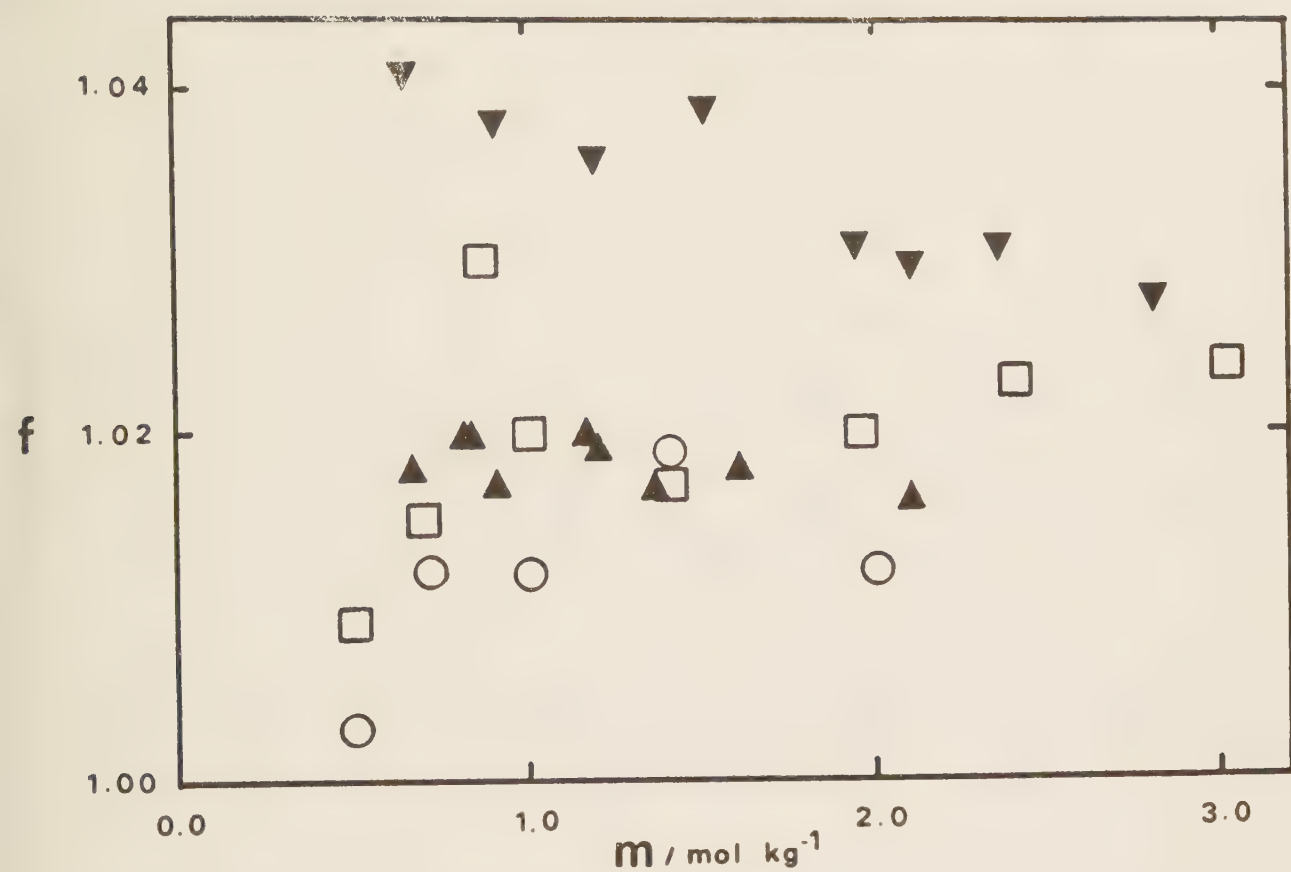


Figure 1. The calculated correction factor f , for heat capacities of NaCl solutions measured with flow microcalorimeters.

○ Picker et al.,⁽¹⁾ □ Fortier et al.,⁽¹¹⁾ ▲ this work -77, ▼ this work -78

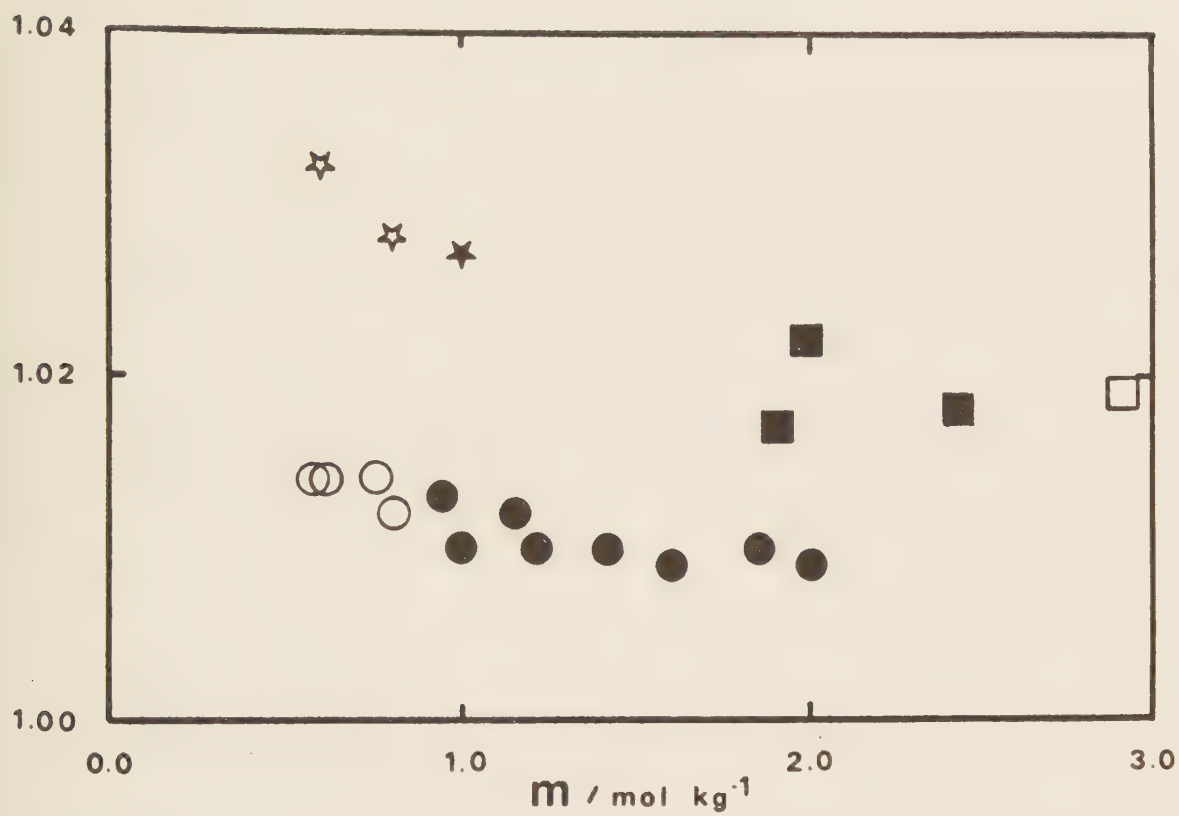


Figure 2. The calculated correction factor f , for heat capacities of KCl and KNO₃ solutions measured with flow microcalorimeters.

★ KCl Fortier et al.,⁽¹¹⁾ ● KCl this work -77, ■ KNO₃ this work -78
Open symbols represent extrapolated values.

Apparent molar heat capacities and volumes of aqueous electrolytes
at 25°C: $\text{Cr}(\text{NO}_3)_3$, LaCl_3 , $\text{K}_3\text{Fe}(\text{CN})_6$, and $\text{K}_4\text{Fe}(\text{CN})_6$

JAN J. SPITZER, INGER V. OLOFSSON,¹ PREM PAUL SINGH,² and
LOREN G. HEPLER

Department of Chemistry, University of Lethbridge
Lethbridge, Alberta, Canada T1K 3M4

-
1. Visiting scientist from Chemical Center, University of Lund, Lund, Sweden.
 2. Visiting scientist from Department of Chemistry, Punjab Agricultural University, Ludhiana, India.

ABSTRACT

We have used a flow calorimeter and a flow densimeter for measurements at 25°C of heat capacities and densities of aqueous solutions of four electrolytes of high charge type: LaCl_3 , $\text{Cr}(\text{NO}_3)_3$, $\text{K}_3\text{Fe}(\text{CN})_6$, and $\text{K}_4\text{Fe}(\text{CN})_6$. Results of these measurements have been used for calculating corresponding apparent molar heat capacities and apparent molar volumes, which have been extrapolated to infinite dilution to obtain the corresponding standard state apparent molar and partial molar properties. Uncertainties resulting from extrapolations of heat capacities are discussed. Results of our measurements are compared with those of earlier related investigations.

Introduction

As part of our continuing program of measurements leading to thermal and volumetric properties of aqueous solutions, we have made calorimetric measurements leading to apparent molar heat capacities and density measurements leading to apparent molar volumes of four electrolytes of high charge type.

These heat capacities and volumes of solutes are useful for calculation of the temperature and pressure dependences of various thermodynamic properties; this usefulness has provided one reason for undertaking these measurements on electrolytes of high charge type, for which there are relatively few reliable volumes and even fewer heat capacities.

It has also been found previously that knowledge of heat capacities and volumes of solute species can help our efforts to understand solute-solvent interactions and the concentration dependence of solute-solute interactions. In this paper we are concerned with the concentration dependence of solute-solute interactions and related limiting slopes, which is a long standing problem for those who have worked with aqueous solutions of electrolytes of high charge type.

Experimental

Heat capacity measurements were made with a flow calorimeter

of the Picker type that has been described previously (1). A small systematic error in some of the measurements has been identified and corrected as recently described (2,3). Densities of solutions have been measured with a flow densimeter that has also been described (4). All results obtained with these instruments refer to $25.00 \pm 0.05^\circ\text{C}$.

A few solutions of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ were prepared by mass from distilled water and BDH Analar salts that had been dried to constant mass at 110°C . Most solutions of these electrolytes were prepared by mass from distilled water and BDH Analar salts that had been recrystallized from distilled water and then dried to constant mass at 105°C .

Fisher certified $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ samples were recrystallized from distilled water and then dissolved in distilled water to form two solutions that were close to 0.1 molar lanthanum chloride with $\text{pH} = 5.3$. Small known amounts of hydrochloric acid were added to these solutions to lower the pH values to 4.9 and 4.3. These solutions were then analyzed gravimetrically for Cl^- by precipitation of AgCl ; allowances were made for the very small amounts of added Cl^- in the calculations of concentrations of lanthanum in the solutions.

Fisher certified $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was recrystallized from dilute nitric acid. Two different samples of the recrystallized material were dissolved in distilled water containing a little

added nitric acid to form stock solutions. Aliquots of these stock solutions were analyzed for chromium as previously described (5). The two stock solutions were found to be 0.1159 molar (pH = 2.2) and 0.3373 molar (pH = 1.2). Further solutions for measurements of heat capacities and densities were prepared by dilution with distilled water; knowledge of densities permitted expression of final composition of solutions in terms of molalities of $\text{Cr}(\text{NO}_3)_3(\text{aq})$.

Results and Discussion

Apparent molar properties of solutions (ϕ_Y) are defined by

$$[1] \quad \phi_Y = [Y(\text{soln}) - n_1 Y_1^0] / n_2$$

in which the symbols have the following means: Y is the property (heat capacity or volume for our purposes) of a specified quantity of solution, n_1 is the number of moles of solvent in this specified quantity of solution, Y_1^0 is the property (heat capacity or volume) of one mole of pure solvent, and n_2 is the number of moles of specified solute in the specified quantity of solution.

Our experimental results (compositions of solutions, heat capacities, densities) have been used to obtain apparent molar heat capacities (ϕ_C) and apparent molar volumes (ϕ_V) that are listed in Table 1. In obtaining these tabulated quantities we have used $c_p^0 = 4.1793 \text{ J K}^{-1} \text{ g}^{-1}$ and $d_1^0 = 0.997044 \text{ g cm}^{-3}$ for the

heat capacity and density of pure water. Rather than tabulate our experimental heat capacities and densities of various solutions, we point out that these quantities can be recovered from the tabulated m , ϕ_C , and ϕ_V values by way of

$$[2] \quad c_p = (m\phi_C + c_p^0)/(1 + mM_2)$$

and

$$[3] \quad d = (1 + mM_2)d_1^0/(1 + md_1^0\phi_V)$$

Apparent molar properties of dilute aqueous solutions of strong electrolytes are accurately described by equations of the form

$$[4] \quad \phi_Y = \phi_Y^0 + A_Y(d_1^0 m)^{1/2} + B_Y m$$

in which ϕ_Y^0 is the limiting value of ϕ_Y at infinite dilution (identical to the corresponding partial molar property $\bar{Y}^0$), A_Y is the limiting slope derived from the Debye-Hückel theory, and B_Y is an adjustable parameter. We begin by applying [4] to our apparent molar volumes and then turn to similar application to our apparent molar heat capacities.

Millero (6) has thoroughly reviewed the applicability of the Debye-Hückel theory to equation [4] to apparent molar volumes and also evaluated the limiting slopes. Following Millero (6) we use $A_V(d_1^0)^{1/2} = 27.413 \text{ cm}^3 \text{ mol}^{-1/2} \text{ kg}^{1/2}$ for electrolytes of 3:1 charge

type and $A_{Vd_1^0}^{1/2} = 58.984 \text{ cm}^3 \text{ mol}^{-3/2} \text{ kg}^{1/2}$ for electrolytes of 4:1 charge type. Least squares analyses of our ϕ_V values in Table 1 in terms of equation [4] leads to the $\phi_V^0 (= \bar{V}^0)$ and B_V values that are summarized in Table 2.

We do not know of any previous measurements on aqueous chromic nitrate leading to a ϕ_V^0 value to compare with our result in Table 2. We can, however, make indirect comparisons of our result with those of earlier workers by way of conventional ionic volumes based on $\phi_V^0(\text{H}^+) = 0$. Using $\phi_V^0(\text{NO}_3^-)$ from Millero (6) with our ϕ_V^0 from Table 2 leads us to our conventional $\phi_V^0(\text{Cr}^{3+}) = -41.6 \text{ cm}^3 \text{ mol}^{-1}$. Millero (6) has previously listed $\phi_V^0(\text{Cr}^{3+}) = -39.5 \text{ cm}^3 \text{ mol}^{-1}$ based on earlier work. Lumme (7) has used densities of relatively concentrated (0.40 to 1.99 molar) solutions of chromic perchlorate to calculate a ϕ_V^0 that we combine with $\phi_V^0(\text{ClO}_4^-)$ from Millero (6) to obtain a conventional $\phi_V^0(\text{Cr}^{3+}) = -47 \text{ cm}^3 \text{ mol}^{-1}$. We judge that our ϕ_V^0 for aqueous chromic nitrate and that our derived conventional $\phi_V^0(\text{Cr}^{3+})$ are the best ones available for this solute.

As shown in Table 2, we have analyzed our results for lanthanum chloride in two ways, obtaining ϕ_V^0 values that differ by $0.5 \text{ cm}^3 \text{ mol}^{-1}$. We judge that the value based only on solutions with $m < 0.04 \text{ mol kg}^{-1}$ is better than the other value, which is based on these results and on those for more concentrated solutions. As can be seen from a graph of our $(\phi_V - 27.413m^{1/2})$

against m , there is a hint of a slight "break" or change in slope in the concentration range near 0.04 mol kg^{-1} . We therefore select $\phi_V = 14.3 \text{ cm}^3 \text{ mol}^{-1}$ as the best value to be obtained from our measurements on aqueous lanthanum chloride and combine with the conventional $\phi_V^0(\text{Cl}^-)$ from Millero (6) to obtain a conventional $\phi_V^0(\text{La}^{3+}) = -39.2 \text{ cm}^3 \text{ mol}^{-1}$.

Dilatometric measurements by Dunn (8) have led him to $\phi_V^0 = 14.28 \text{ cm}^3 \text{ mol}^{-1}$ for aqueous lanthanum chloride. Density measurements by two methods have led Spedding et al. (9,10) to report $\phi_V^0 = 14.51$ to $14.688 \text{ cm}^3 \text{ mol}^{-1}$ for aqueous lanthanum chloride; we judge the first of these values to be better than the second because the first is based on densities for more dilute solutions than is the second.

We can also compare our conventional $\phi_V^0(\text{La}^{3+})$ from aqueous lanthanum chloride with similar conventional $\phi_V^0(\text{La}^{3+})$ values derived from ϕ_V^0 values for other salts of lanthanum. Results of this comparison, for which we have used $\phi_V^0(\text{Cl}^-)$, $\phi_V^0(\text{ClO}_4^-)$, and $\phi_V^0(\text{NO}_3^-)$ from Millero (6), are presented in Table 3. On the basis of our assessments of all of the investigations cited in Table 3, with particular bias in favor of ϕ_V^0 values

on the most dilute solutions, we choose $\phi_V^0(\text{La}^{3+}) = -39.1$ as the best available conventional ionic volume for $\text{La}^{3+}(\text{aq})$ at 25°C .

For aqueous $\text{K}_3\text{Fe}(\text{CN})_6$, a 3:1 electrolyte, we have $\phi_V^0 = 14.4$.

146.2 and 146.8 $\text{cm}^3 \text{mol}^{-1}$ from previous investigations (16-18), all in excellent agreement with our present $\phi_V^0 = 146.6 \text{ cm}^3 \text{mol}^{-1}$.

Previous investigations of aqueous $\text{K}_4\text{Fe}(\text{CN})_6$, a 4:1 electrolyte, have led to the following. Hepler, Stokes, and Stokes (18) obtained $\phi_V^0 = 110 \text{ cm}^3 \text{mol}^{-1}$ by way of measurements with a dilatometer. More recently, Billi et al. (16) have reported $\phi_V^0 = 108.5 \text{ cm}^3 \text{mol}^{-1}$, based on similar measurements; it is desirable to recalculate their results by way of an equation like [4], but their results are not presented in a way that permits such recalculation. Still other dilatometric measurements by Curthoys and Matheson (17) have led them to report $\phi_V^0 = 112.3 \text{ cm}^3 \text{mol}^{-1}$; our recalculation (omitting the ϕ_V for their most dilute solution, for reasons discussed by Curthoys and Matheson) leads us to $\phi_V^0 = 112.7 \text{ cm}^3 \text{mol}^{-1}$. Our present $\phi_V^0 = 113.3 \text{ cm}^3 \text{mol}^{-1}$ is not in ideal agreement with any of the previous results, which are not in good agreement with one another. There is no present way to make a rational selection of a best ϕ_V^0 for aqueous $\text{K}_4\text{Fe}(\text{CN})_6$.

Previous experience here and elsewhere with flow densimeters of the type we have used has provided good evidence that total uncertainties in derived ϕ_V^0 values are usually less than $\pm 0.5 \text{ cm}^3 \text{mol}^{-1}$. The agreement of our present ϕ_V^0 values for aqueous LaCl_3 (see Table 3) and aqueous $\text{K}_3\text{Fe}(\text{CN})_6$ (discussed in the text earlier) is consistent with a similar estimate of our present uncertainties in ϕ_V^0 values for these solutes.

Because previous results for salts of $\text{Cr}^{3+}(\text{aq})$ have quite large uncertainties, we are unable to use comparisons as a guide in estimating the uncertainty in our $\varnothing_V^0$ for aqueous $\text{Cr}(\text{NO}_3)_3$. Instead, we estimate that the uncertainties in our density measurements are about the same as for other solutions, and also recognize that there is an additional source of uncertainty in the derived $\varnothing_V$ and $\varnothing_V^0$ values. Because of the tendency of $\text{Cr}^{3+}(\text{aq})$ to hydrolyze to such species as $\text{CrOH}^{3+}(\text{aq})$, it was necessary for us to work with solutions that contained ~~some~~ nitric acid as well as the chromic nitrate of interest to us. The resulting additional uncertainty associated with treatment of our experimental data leads us to estimate that the total uncertainty in our reported $\varnothing_V^0$ for aqueous $\text{Cr}(\text{NO}_3)_3$ is about $\pm 1.2 \text{ cm}^3 \text{ mol}^{-1}$.

Uncertainties in $\varnothing_V^0$ values based on dilatometric measurements of the type used in the three earlier investigations (16-18) of aqueous $\text{K}_4\text{Fe}(\text{CN})_6$ are typically less than $\pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$, as they are for the flow densimeter we have used. It is obvious from the range of reported values (108.5, 110, 112.3 or 112.7, and $113.3 \text{ cm}^3 \text{ mol}^{-1}$) that true uncertainties for at least some of these results are larger than normally found in this kind of work. We have no reliable way of selecting the best value or of assessing individual uncertainties.

In connection with our previous investigations of heat capacities of aqueous electrolytes of charge types 1:1 and 2:1 we

have used $A_C(d_1^0)^{1/2} = 28.95$ and $150.4 \text{ J K}^{-1} \text{ mol}^{-3/2} \text{ kg}^{1/2}$. These values are based on the earlier analyses of Philip and Desnoyers (19) and Leduc, Fortier, and Desnoyers (20), and have been used in connection with many similar investigations at the Université de Sherbrooke and elsewhere. Calculations by Spitzer (22) and by Silvester and Pitzer (23) have led to values of $A_C(d_1^0)^{1/2}$ about 10% and about 25% larger, respectively, than the values quoted above. Nearly all of the differences between these limiting slopes can be attributed to differences in the second derivatives of the dielectric constant of water with respect to temperature that have been selected by the various investigators (19,20,22,23). Desnoyers et al. (19-21) and Spitzer (22) have tried to obtain the best limiting slopes for 25°C and other "ordinary" temperatures, all at 1 atm, while Silvester and Pitzer (23) have tried (24) to obtain the best complete set of limiting slopes for a much wider range of temperatures and pressures. These different approaches have necessarily been substantially based on different sets of dielectric constants and have therefore led to different second derivatives, which accounts for part of the discrepancy in $A_C(d_1^0)^{1/2}$ values.

If it were possible to make heat capacity measurements of sufficient accuracy on very dilute solutions, it would then be possible to obtain accurate ϕ_C^0 values and also limiting slopes by simply plotting ϕ_C against $m^{1/2}$. Since this simple approach is made

unsatisfactory by our inability to make sufficiently accurate heat capacity measurements on sufficiently dilute solutions, we are forced to make use of some approach based on an equation like [4]. Application of equation [4] with three adjustable parameters (ϕ_C , A_C , and B_C) to presently available heat capacities is generally unsatisfactory because it is possible to fit the experimental results with a range of values of the three parameters that is unacceptably large. We note, however, that modest improvements in our ability to measure heat capacities of dilute solutions may suffice to make one of the approaches described in this paragraph useful in the future.

Our best presently available approach to analysis of heat capacities of dilute solutions is based on equation [4] with limiting slope derived from the Debye-Hückel theory and the properties (density and dielectric constant) of water. In our following discussion of this approach, we will focus on the slopes from Desnoyers et al. (19,20) and from Silvester and Pitzer (23) because Spitzer's limiting slope falls in between these other values.

Application (25) of equation [4] to typical heat capacities of 1:1 electrolytes at 25°C is not critically dependent on whether we use Desnoyers' (19,20) or Pitzer's (23) limiting slope because derived ϕ_C^0 values ordinarily differ by only about $1 \text{ J K}^{-1} \text{ mol}^{-1}$, which is about one-third of the commonly estimated uncertainty

associated with heat capacities obtained recently in both Sherbrooke and Lethbridge. Similar application (25) of equation [4] to heat capacities of solutions of 2:1 electrolytes shows that $\varnothing_C^0$ values derived on the basis of the two different limiting slopes under present consideration differ by about $6 \text{ J K}^{-1} \text{ mol}^{-1}$, which is a little larger than previously estimated uncertainties in these values. Because of the way (19,20,22,23) in which electrolyte charge enters A_C , we anticipate that the $\varnothing_C^0$ values derived from applications of equation [4] to our present heat capacities of solutions of electrolytes of 3:1 and 4:1 charge types will depend significantly on our choice of limiting slope.

Our calculations with equation [4] for 3:1 electrolytes have been based on $A_C(d_1^0)^{1/2} = 425.5$ and $523 \text{ J K}^{-1} \text{ mol}^{-3/2} \text{ kg}^{1/2}$ from Desnoyers et al. (19,20) and from Silvester and Pitzer (23), respectively. Similar calculations for the 4:1 electrolyte $\text{K}_4\text{Fe}(\text{CN})_6$ have been done with $A_C(d_1^0)^{1/2} = 915.5$ and $1126 \text{ J K}^{-1} \text{ mol}^{-3/2} \text{ kg}^{1/2}$ from the same sources. Results of all of these calculations are summarized in Table 4.

We do not know of any heat capacities of solutions of $\text{Cr}(\text{NO}_3)_3$, $\text{K}_3\text{Fe}(\text{CN})_6$, or $\text{K}_4\text{Fe}(\text{CN})_6$ that can be compared with our results in Tables 1 and 4.

Spedding and Jones (26) have measured heat capacities of aqueous solutions of lanthanum chloride, all having molalities greater than 0.1 mol kg^{-1} , and have treated their results with an

equation of the form of

$$[5] \quad \phi_C = \phi_C^0 + A m^{1/2} + B m + C m^{3/2} + D m^2$$

in which A, B, C, and D are adjustable parameters. They report $\phi_C^0 = -466 \text{ J K}^{-1} \text{ mol}^{-1}$. It is our opinion that the uncertainty in this value (mostly due to uncertainty in the data treatment) is too large to justify its use in choosing between the various ϕ_C^0 values listed for aqueous LaCl_3 in Table 4.

We also note that heat capacities of solutions of $\text{La}(\text{NO}_3)_3$ and $\text{La}(\text{ClO}_4)_3$ have been measured (27,28) at concentrations above 0.1 mol kg^{-1} . Extrapolations of the results to infinite dilution by way of equations like [5] have led (27,28) to $\phi_C^0 = -286 \text{ J K}^{-1} \text{ mol}^{-1}$ for aqueous $\text{La}(\text{NO}_3)_3$ and to $\phi_C^0 = -222 \text{ J K}^{-1} \text{ mol}^{-1}$ for aqueous $\text{La}(\text{ClO}_4)_3$. Combinations of these values with conventional ϕ_C^0 values (29) for aqueous Cl^- , NO_3^- , and ClO_4^- leads to $\phi_C^0 = -448$ and $-525 \text{ J K}^{-1} \text{ mol}^{-1}$ for aqueous LaCl_3 . Again we are unable to use these results from other investigations to help us choose between the various ϕ_C^0 values listed in Table 4.

Heat capacities of solutions of a few other MCl_3 salts are worth mentioning. Measurements by Vasilev et al. (30,31) have led to $\phi_C^0 = -418 \text{ J K}^{-1} \text{ mol}^{-1}$ for aqueous YCl_3 and to $\phi_C^0 = -466 \text{ J K}^{-1} \text{ mol}^{-1}$ for aqueous CeCl_3 . Spedding, Walters, and Baker (32) have measured heat capacities of solutions of eight different rare earth chlorides and have reported corresponding ϕ_C^0 values ranging

from -434 to $-519 \text{ J K}^{-1} \text{ mol}^{-1}$; we particularly note their $\phi_C^0 = -493 \text{ J K}^{-1} \text{ mol}^{-1}$ for aqueous GdCl_3 . Jekel, Criss, and Cobble (33) have used enthalpies of solution at several temperatures to derive $\phi_C^0 = -435 \text{ J K}^{-1} \text{ mol}^{-1}$ for aqueous GdCl_3 at 25°C . Once again we are unable to use these results from other investigations to help us choose between the various ϕ_C^0 values listed in Table 4.

In spite of the uncertainties in our measurements and those from our calculations based on different limiting slopes in the heat capacity equation [4], we believe that our ϕ_C^0 values in Table 4 are the best ones now available for aqueous electrolytes of 3:1 and 4:1 charge types.

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TABLE 1. Apparent molar heat capacities and volumes

m	ρ_C	ρ_V	m	ρ_C	ρ_V
mol kg ⁻¹	J K ⁻¹ mol ⁻¹	cm ³ mol ⁻¹	mol kg ⁻¹	J K ⁻¹ mol ⁻¹	cm ³ mol ⁻¹
LaCl ₃			Cr(NO ₃) ₃ [*]		
0.013967	-419.7	17.05	0.01738	-206.5	48.36
0.017906	-415.1	17.05	0.02316	-215.7	48.83
0.018609	-410.9	16.56	0.03477	-225.5	48.69
0.026898	-417.2	16.83	0.04638	-231.5	49.23
0.027946	-412.1	17.31	0.05807	-225.9	49.57
0.027949	-406.6	17.77			
0.035838	-408.4	17.34	0.03370	-223.6	49.81
0.037227	-403.8	17.73	0.05057	-229.4	49.12
0.037231	-409.0	17.51	0.06740	-226.6	49.66
0.044908	-404.0	17.92	0.1012	-224.7	49.67
0.046625	-401.7	17.97	0.1350	-219.1	49.93
0.053826	-398.6	17.81	0.1690	-213.4	49.97
0.071695	-393.5	18.32			
0.089901	-386.8	18.65	K ₄ Fe(CN) ₆		
0.089901	-386.7	18.70	0.007526	-383.1	117.53
K ₃ Fe(CN) ₆			0.013040	-362.8	119.10
			0.022280	-337.8	120.76
0.02003	-152.6	149.49	0.024516	-330.1	121.97
0.03105	-141.2	151.43	0.029576	-324.4	122.60
0.04863	-126.8	152.02	0.034545	-312.2	123.58
0.06025	-119.9	151.62	0.041080	-311.6	123.25
0.08212	-109.8	151.97	0.049830	-287.6	125.09
0.10299	-100.0	152.73	0.070083	-273.0	125.55
0.15588	-85.7	153.88	0.079670	-254.4	125.82
			0.099630	-232.4	129.39
			0.13219	-218.8	128.07

* Stock solution for the first five measurements was 0.1159 molar Cr(NO₃)₃ and had initial pH = 2.2; stock solution for the last six measurements was 0.3373 molar Cr(NO₃)₃ and had initial pH = 1.2. In both cases, solutions used in the measurements were prepared by dilution with distilled water.

TABLE 2. Volumetric parameters for equation [4]

Solute	ϕ_V^0 cm ³ mol ⁻¹	B_V cm ³ mol ⁻² kg
Cr(NO ₃) ₃	45.4	-41.1
K ₃ Fe(CN) ₆	146.6	-24.6
LaCl ₃ (all points)	13.8	-39.4
(m < 0.04)	14.3	-54.9
K ₄ Fe(CN) ₆	113.3	-43.4

TABLE 3. Conventional $\phi_V^0(\text{La}^{3+})$ values

$\phi_V^0(\text{La}^{3+})$ $\text{cm}^3 \text{ mol}^{-1}$	Solute	Source
-39.7	LaCl_3	This work, all points
-39.2	LaCl_3	This work, $m < 0.04$
-39.2	LaCl_3	Ref. (8)
-39.0	LaCl_3	Ref. (9)
-38.8	LaCl_3	Ref. (10)
-39.0	$\text{La}(\text{ClO}_4)_3$	Ref. (11)
-38.8	$\text{La}(\text{ClO}_4)_3$	Ref. (12)
-37	$\text{La}(\text{ClO}_4)_3$	Ref. (13)
-37.6	$\text{La}(\text{NO}_3)_3$	Ref. (9)
-37.5	$\text{La}(\text{NO}_3)_3$	Ref. (14)
39	$\text{La}(\text{NO}_3)_3$	Ref. (15)

TABLE 4: Heat capacity parameters for equation [4]

Solute	Desnoyers' limiting slope		Pitzer's limiting slope	
	ϕ_C^0	B_C	ϕ_C^0	B_C
	J K ⁻¹ mol ⁻¹	J K ⁻¹ mol ⁻² kg	J K ⁻¹ mol ⁻¹	J K ⁻¹ mol ⁻² kg
LaCl ₃ all points	-465	-580	-475	-805
m < 0.04	-456	-898	-464	-1203
Cr(NO ₃) ₃ m < 0.04	-223	-2337	-231	-2644
m < 0.06	-242	-1628	-251	-1887
visual	-230		-240	
K ₃ Fe(CN) ₆	-206.5	-300	-218.7	-478
K ₄ Fe(CN) ₆	-460	-688	-481	-1141

The main aim of the work discussed in the present summary has been to obtain basic thermodynamic information of water and aqueous electrolyte solutions.

The enthalpy of ionization of water between 273 and 418 K has been determined calorimetrically (papers I-III). The results are used to evaluate an equation of ΔC_p^O as a function of temperature, leading to equations for the temperature dependence of ΔH_i^O and K_w^O . Heat capacity measurements on NaCl, KCl, and KNO_3 solutions up to 3 mol kg⁻¹ have been made with one LKB reaction-solution calorimeter and two Picker flow micro-calorimeters to check the accuracy of the flow calorimetric measurements (paper IV). Apparent molar heat capacities and apparent molar volumes, at constant pressure and 298.15 K, have been determined for 28 aqueous electrolytes for charge types 1:1, 2:1, 3:1, and 4:1 (papers V-IX).

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Can. J. Chem. Submitted.

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1. Introduction

BASIC THERMODYNAMIC EQUATIONS AND DEFINITIONS

Both in "pure" and "applied" chemistry, it is of primary interest to have a good thermodynamic description of a process. That can be achieved by the use of a small number of thermodynamic properties.

The ionization of water can be described by the relation:



The thermodynamic equilibrium constant in terms of activities is

$$K_w^0 = (a_{\text{H}^+})(a_{\text{OH}^-})/(a_{\text{H}_2\text{O}}) \quad (2)$$

with the activities commonly based on the following standard state conditions. The standard state of $\text{OH}^- (aq)$ and $\text{H}^+ (aq)$ is the hypothetical one of an ideal (infinitely dilute) solution of standard-state molality (1 mol kg^{-1}) and at the standard-state pressure ($101\,325 \text{ Pa}$), which is also the standard state used in this work. The standard state for $\text{H}_2\text{O}(l)$ is that of the pure liquid water under the standard-state pressure $101\,325 \text{ Pa}$. Hence $a_{\text{H}_2\text{O}}$ is equal unity and the standard equilibrium constant K_w^0 can be written as:

$$K_w^0 = a_{\text{H}^+} \cdot a_{\text{OH}^-} \quad (3)$$

The thermodynamic properties of most interest are:

The standard free energy change ΔG_1^0 , which can be derived from K_w^0 using the relation:

$$\Delta G_1^0 = -RT \ln K_w^0 \quad (4)$$

The standard enthalpy change ΔH_1^0 , which relates to the temperature dependence of K_w^0 in the following way:

$$\Delta H_1^0 = -R \, d \ln K_w^0 / d(1/T) \quad (5)$$

$$\Delta H_1^0 = RT^2 \, d \ln K_w^0 / dT \quad (6)$$

The standard heat capacity change ΔC_p° , which is equal to the temperature derivative of ΔH_i° :

$$\Delta C_p^{\circ} = d\Delta H_i^{\circ}/dT \quad (7)$$

The standard entropy change ΔS_i° , which is equal to the negative temperature derivative of ΔG_i° :

$$\Delta S_i^{\circ} = -d\Delta G_i^{\circ}/dT \quad (8)$$

Finally we have the volume change ΔV_i , which is equal to the pressure derivative of ΔG_i° :

$$\Delta V_i = d\Delta G_i^{\circ}/dP \quad (9)$$

CALCULATION OF ΔH_i° AND ΔC_p° FROM VALUES OF K_w°

How useful are values of the equilibrium constant for calculating other thermodynamic properties?

The equilibrium constant is the property which has been most studied over a wide temperature range. A plot of pK_w° versus $1/T$ is shown in figure 1. At $1/T = 1.9 \cdot 10^{-3} \text{ K}^{-1}$,

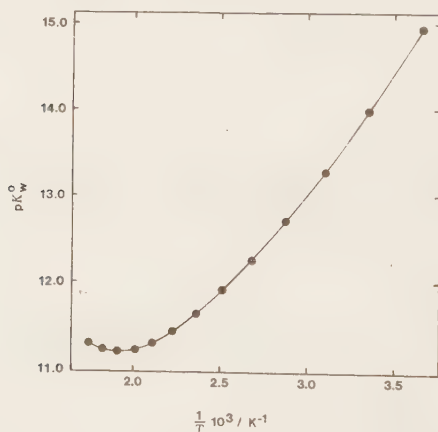


Figure 1. The standard equilibrium constant for the ionization of water.

corresponding to the temperature 520 K, pK_w^O goes through a minimum. Hence the enthalpy of ionization of water is zero at this temperature, positive below, and negative at higher temperatures.

Timini ⁽¹⁾ has discussed the propagation of error when using values of K_w^O to derive ΔC_p^O values, and I will only give a simplified example. From a set of $\log K_w^O$ values I have calculated the average ΔH_i^O of each temperature interval using equation (6), where T is the average temperature of each interval. From reference (2) I have used $\log K_w^O = -14.941 \pm 0.009$ at 273.15 K, $\log K_w^O = -13.993 \pm 0.009$ at 298.15 K, and $\log K_w^O = -13.272 \pm 0.006$ at 323.15 K. The average enthalpy change of each temperature interval then became $\Delta H_i^O = 59.25 \pm 0.80$ and 53.28 ± 0.79 kJ mol⁻¹ for the average temperatures 285.65 and 310.65 K, respectively. These ΔH_i^O values were used to calculate the average heat capacity change at 298.15 K and the result was $\Delta C_p^O = -238 \pm 45$ J K⁻¹ mol⁻¹. Thus the uncertainty introduced by a small error in the equilibrium constant is magnified by each derivation and, even though the equilibrium constant is determined very accurately, the uncertainty of the derived values increases rapidly. Timini ⁽¹⁾ concluded from his computational work that, in order to derive reliable values of ΔC_p from pK values, a large number of very accurate measurements extended over a large temperature range (more than 100 K) is needed.

USE OF ΔH_i^O AND ΔC_p^O FOR EXTRAPOLATIONS

One useful application of thermodynamics is the calculation of the equilibrium constant and other thermodynamic functions over a wide range of temperature from results of measurements made over a smaller range.

An empirical equation for the equilibrium constant as a function of temperature can be used, with confidence, only in a very narrow range outside the temperature range of the measurements. If we know the temperature derivative, that

is if we know the enthalpy change, these calculations can be extended over a larger interval. The equilibrium constant can be calculated at a temperature T_2 from values of $\ln K_w^0$ and ΔH_i^0 at a nearby temperature by use of the relation:

$$\ln K_w^0(T_2) = \ln K_w^0(T_1) + 1/R \int_{T_1}^{T_2} (\Delta H_i^0/T^2) dT \quad (10)$$

The same is valid for the enthalpy change; we can use a heat capacity change with an enthalpy change at one temperature to calculate the enthalpy changes at other nearby temperatures using the equation:

$$\Delta H_i^0(T_2) = \Delta H_i^0(T_1) + \int_{T_1}^{T_2} \Delta C_p^0 dT \quad (11)$$

If we know something about the variation of ΔC_p^0 with temperature we can extend these calculations of enthalpy changes, and consequently the equilibrium constant, to considerably higher and lower temperatures.

A similar discussion is applicable for the pressure dependence of ΔG , and thus K_w . Using data on volume changes ΔG can be calculated at pressures outside the range over which the measurements were made by the use of the relation:

$$\Delta G(P_2) = \Delta G(P_1) + \int_{P_1}^{P_2} \Delta V dP \quad (12)$$

2. The ionization of water

BACKGROUND

Several investigations are made, especially around room temperature, leading to values of the enthalpy change of the ionization of water.

When evaluating the consistency of the data on enthalpy changes it is convenient to do it by way of the differences $(\Delta H_T^{\circ} - \Delta H_{298.15}^{\circ}) / (T - 298.15)$ as is discussed by Hepler and Woolley.⁽³⁾ Such differences calculated from values of ΔH_1° reported in the literature up to 1972⁽⁴⁻¹²⁾ are plotted versus $(T - 298.15)$ in figure 2.

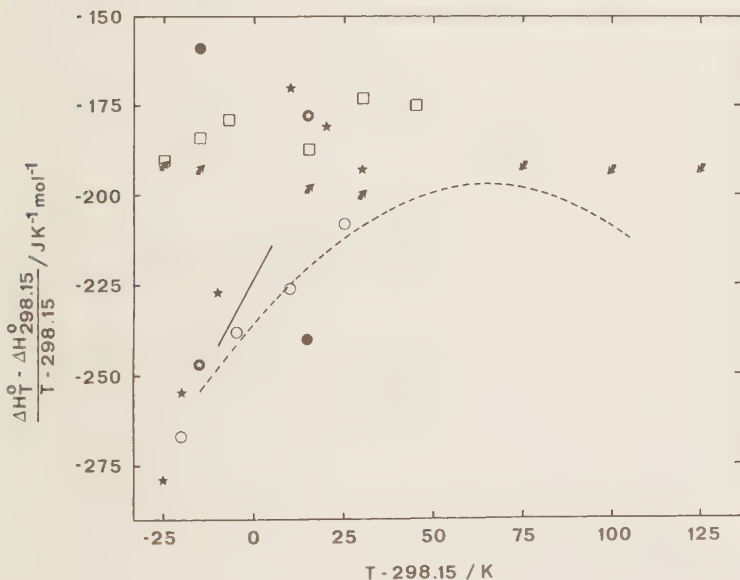


Figure 2. Ionization of water.

----- Ackermann, — Parker, ○ Grenthe, ⊛ Christensen,
 ● Anderson, □ Vasil'ev, ★ Leung, ⦿ Harned, ▲ Dobson.

The dotted line is based on heat capacity measurements on NaOH and HCl solutions reported by Ackermann.⁽⁴⁾ Heat capacity data on NaOH and HCl solutions in the compilation by Parker⁽⁵⁾ have been used to calculate the enthalpy changes which are represented by the solid line. Anderson et al.,⁽⁶⁾ Vasil'ev and Lobanov,⁽⁷⁾ Leung and Grunwald,⁽⁸⁾ Grenthe et al.,⁽⁹⁾ and Christensen et al.⁽¹⁰⁾ report results from calorimetric measurements of the enthalpy of neutralization of a strong acid with a strong base. The enthalpy changes at infinite dilution were determined, either by extrapolation of the experimental enthalpy changes to zero concentration, or by correcting them with calculated enthalpies of dilution. Grenthe et al.⁽⁹⁾ also measured the enthalpy of dilution of the acid and then used Parkers⁽⁵⁾ enthalpy of dilution data and Ackermanns⁽⁴⁾ heat capacity data to correct their experimental results to standard state conditions. Harned and Owen⁽¹¹⁾ and Dobson and Thirsk⁽¹²⁾ made electrochemical investigations leading to values of the equilibrium constant for ionization of water at various temperatures and from which they derived the enthalpy changes.

As can be seen from figure 2, there is a big discrepancy between the results from different investigations. Values of $(\Delta H_T^{\circ} - \Delta H_{298.15}^{\circ}) / (T - 298.15)$ range from - 160 to - 280 J K⁻¹ mol⁻¹, making it difficult to select a best value, or to derive some function describing the temperature dependence of ΔH_1° . Hepler and Woolley⁽³⁾ derived the following polynomial to express ΔH_1° as a function of temperature:

$$\Delta H_T^{\circ} / \text{cal mol}^{-1} = 69,283 - 321.8 T + 0.45 T^2 \quad (13)$$

in which the heat capacity data derived by Parker⁽⁵⁾ was given heavy weight.

CALORIMETRIC DETERMINATION OF ΔH_1° BETWEEN 273 AND 418 K (PAPERS I, II, III)

The results reported by different investigators show considerable discrepancies (see figure 2). To improve our knowledge of the thermodynamics

of the ionization of water, we have determined the enthalpy changes from 273 K to 418 K.

The enthalpy of ionization of water has been determined by measurements of the enthalpy of neutralization of HCl with excess NaOH. The large discrepancies between the results reported by different investigators (see figure 2) may partly be due to errors introduced in reducing the experimental results to standard-state conditions. To minimize the influence of uncertainties in the dilution corrections we chose to use as dilute solutions as was judged possible.

Measurements from 298 to 418 K (paper I) were made with an LKB reaction-solution rotating-bomb calorimeter. The experiments were carried out by addition of 0.8 g HCl solution of molality 2.1 mol kg^{-1} to 60 g 0.05 mol kg^{-1} NaOH solution. The enthalpy of dilution of 0.8 g 2.1 mol kg^{-1} HCl into 60 g water was also measured at each temperature.

In the experiments between 273 and 323 K (paper II) we used a 100 cm^3 glass reaction vessel and the experiments were carried out by adding 0.8 g HCl of molality 0.50 mol kg^{-1} to 100 g of 0.01 mol kg^{-1} NaOH. The enthalpy of dilution of 0.8 g HCl solution in 100 g water was also measured at each temperature. A modified reaction-solution rotating-bomb calorimeter with air thermostat is reported on in paper III. The enthalpy of neutralization of 0.51 mol kg^{-1} HCl in excess NaOH was measured at 298, 373, and 415 K. The molality of the NaOH solution was $0.020 \text{ mol kg}^{-1}$ in the experiments at 298.15 and 373.65 K and $0.015 \text{ mol kg}^{-1}$ at 415.15 K. Previously determined enthalpies of dilution of 0.5 mol kg^{-1} HCl in water were used. ⁽¹³⁾

To reduce our experimental enthalpy changes to standard-state conditions, at 298.15 K, the dilution correction to infinite dilute solution was calculated using the enthalpies of dilution from Parker's compilation. ⁽⁵⁾ At the other temperatures the corrections were calculated by graphical integration using Ackermann's ⁽⁴⁾ heat capacity results. For the results in paper I, the sum of the dilu-

tion corrections estimated in this way became 0.5 % of the enthalpy of neutralization at 323 K. With increasing temperature the correction increased, and at 418 K it was 3.3 %. When using HCl of molality 0.5 mol kg^{-1} the corresponding correction became considerably smaller. For the enthalpy changes reported in paper II it ranged from 0.1 % at 273 K to 0.2 % at 323 K, and for the enthalpy changes reported in paper III the correction was 0.8 % at 373 K and 1.3 % at 415 K.

The results from our calorimetric determinations of the enthalpy of ionization of water are summarized in table 1, where n denotes the number of neutralization experiments carried out. Error limits are expressed as twice the standard deviation of the mean. Estimates of uncertainties in the dilution corrections, at other temperatures than 298.15 K, are not included except for the results from paper III.

Table 1. Enthalpies of ionization of water.

n	T K	ΔH_i^0 kJ mol^{-1}	$2s$	n	T K	ΔH_i^0 kJ mol^{-1}	$2s$
Paper I				Paper II			
5	298.15	55.92	0.11	5	273.70	62.13	0.11
5	323.40	50.92	0.09	5	284.85	58.94	0.14
4	347.55	46.67	0.10	6	298.15	55.84	0.14
4	373.55	42.07	0.12	5	305.65	54.28	0.08
4	328.45	37.35	0.13	6	313.15	52.81	0.24
3	417.75	33.45	0.13	5	323.15	51.01	0.17
Paper III							
8	298.15	55.72	0.30				
6	373.65	41.74	0.60				
6	415.15	33.46	0.50				

Our results represented as $(\Delta H_T^\circ - \Delta H_{298.15}^\circ)/(T - 298.15)$ are shown in figure 3 together with the values at 298.15 reported in the literature. (4,5,7,9,10,14-17)

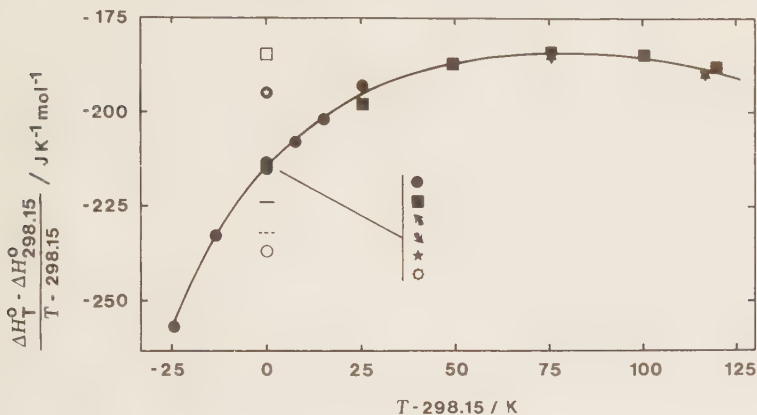


Figure 3. Ionization of water.

● ■ ★ Present work, □ Vasil'ev, ⊛ Christensen, ▩ Singh, ▨ Singh, ★ Enea, ⊙ Allred, — Parker, --- Ackermann, ○ Grenthe.

From figure 3 it can be seen that our results vary smoothly, which indicates that ΔC_p° values calculated from our values of ΔH_1° will show a consistent behaviour.

DETERMINATION OF ΔC_p° OF IONIZATION OF WATER

Values of the standard heat capacity change of the ionization of water are calculated from the unsmoothed values of the enthalpy change.

The values of ΔC_p° given in paper I were calculated, from our derived equation for ΔH_1° as a function of temperature, by differentiation with respect to temperature. This method, of calculating values of ΔC_p° from the already smoothed ΔH_1° values, leads to unnecessarily large distortions, due to the "smoothing-in" of incoherent errors, as is discussed in detail in reference 19. In the present

work we have chosen to follow the recommendation "Differentiate then smooth; never smooth then differentiate" given in reference 19/ and calculated values of ΔC_p^O from the unsmoothed ΔH_i^O values by semigraphical differentiation.

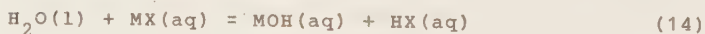
The values of ΔC_p^O derived from the results in papers I and II are listed in the second and third columns of table 2. The random errors are expressed as the estimated standard deviation of the mean.

Table 2. ΔC_p^O of ionization of water.

T / K-273.15	$\Delta C_p^O / J K^{-1} mol^{-1}$	
	paper I	paper II
0		-325 $\pm$ 10
10		-265 $\pm$ 8
15		-245 $\pm$ 7
25	-213 $\pm$ 5	-214 $\pm$ 5
30	-207 $\pm$ 5	-203 $\pm$ 7
40	-194 $\pm$ 5	-187 $\pm$ 8
50	-183 $\pm$ 7	-175 $\pm$ 10
70	-174 $\pm$ 7	
90	-178 $\pm$ 8	
110	-188 $\pm$ 8	
130	-199 $\pm$ 9	
150	-211 $\pm$ 10	

The standard heat capacity change of the ionization of water can also be calculated from values of the partial molar heat capacity of aqueous electrolytes.

If we write the reaction for the ionization of water as:



we get the standard heat capacity change as:

$$\Delta C_p^{\circ} = C_p^{\circ}(\text{MOH}) + C_p^{\circ}(\text{HX}) - C_p^{\circ}(\text{MX}) - C_p^{\circ}(\text{H}_2\text{O}) \quad (15)$$

At 298.15 K several flow micro-calorimetric investigations⁽¹⁴⁻¹⁷⁾ have been made leading to ΔC_p° of ionization of water. A best value of $\Delta C_p^{\circ} = -215.2 \text{ J K}^{-1} \text{ mol}^{-1}$ (estimated uncertainty of $\pm 4 \text{ J K}^{-1} \text{ mol}^{-1}$) was recommended by Singh et al.⁽¹⁴⁾ from results of their investigation of eight 1:1 electrolytes. Heat capacity measurements of various electrolytes have led Singh et al.⁽¹⁵⁾ to $\Delta C_p^{\circ} = -213.8 \text{ J K}^{-1} \text{ mol}^{-1}$, Enea et al.⁽¹⁶⁾ to $\Delta C_p^{\circ} = -214.6 \text{ J K}^{-1} \text{ mol}^{-1}$, and Allred and Woolley⁽¹⁷⁾ to $\Delta C_p^{\circ} = -217.0 \text{ J K}^{-1} \text{ mol}^{-1}$. The results from these flow calorimetric measurements agree very well with each other and with ours as well (see figure 3). The average value, $\Delta C_p^{\circ} = -215.2 \text{ J K}^{-1} \text{ mol}^{-1}$, from flow calorimetric measurements has been chosen as the best value at 298.15 K.

Allred and Woolley⁽¹⁷⁾ have also made measurements at 283.15 and 313.15 K leading to $\Delta C_p^{\circ} = -261.2$ and $-193.4 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. These values can be compared with our $\Delta C_p^{\circ} = -265 \text{ J K}^{-1} \text{ mol}^{-1}$ at 283.15 K and $\Delta C_p^{\circ} = -187 \text{ J K}^{-1} \text{ mol}^{-1}$ at 313.15 K.

EQUATION FOR ΔC_p° OF IONIZATION OF WATER AS A FUNCTION OF TEMPERATURE

The values of the standard heat capacity change of the ionization of water, which we have judged as the best, now available, have been used to derive an equation to describe the temperature dependence of the heat capacity change.

Our calorimetric measurements (papers I-III) have led to values of ΔC_p° at the average temperature of two consecutive determinations of ΔH_1° . The ΔC_p° values are shown in figure 4 and table 3, together with the results from flow-calorimetric measurements at 283.15 and 313.15 K⁽¹⁷⁾ and 298.15 K.⁽¹⁴⁻¹⁷⁾ These ΔC_p° values were fitted by a least squares method to the equation

$$\Delta C_p^{\circ} = a + bT + c \cdot (T-d)^{-2} \quad (16)$$

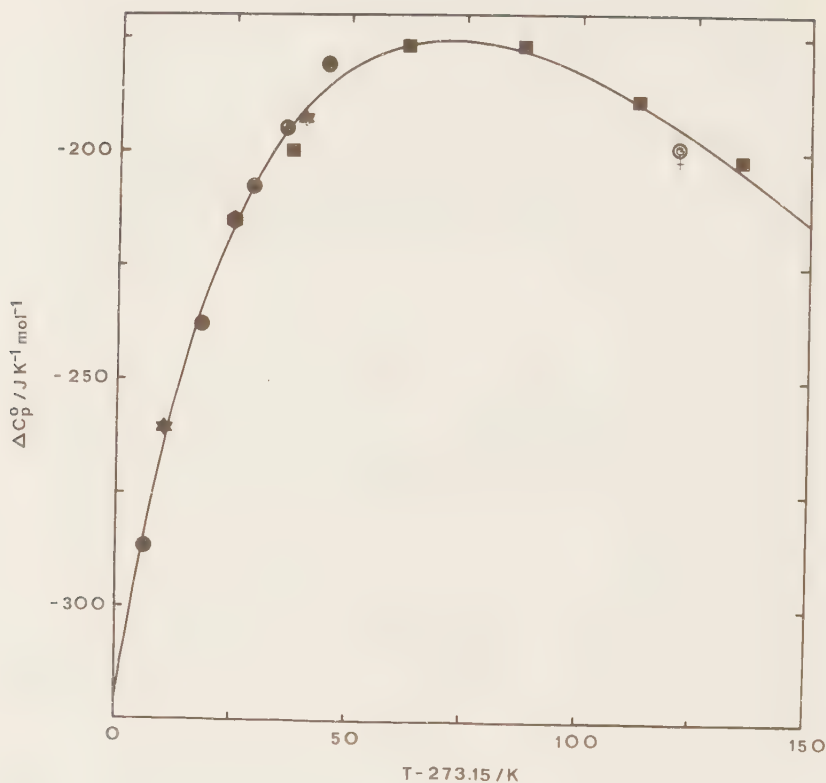


Figure 4. ΔC_p^0 of ionization of water.

■ paper I, ● paper II, ⊗ paper III, ★ Allred,
 ⊕ Singh, Singh, Enea, Allred.

which is a modified form of an equation commonly used to express the temperature dependence of ΔC_p .⁽²⁰⁾

In the fitting all values were given equal weight except the value at 298.15 K which was given double weight.

The following equation was found to represent the data accurately:

$$\Delta C_p^{\circ} / \text{J K}^{-1} \text{ mol}^{-1} = 285.0 - 1.1016 T - 1.7689 \cdot 10^6 (T-197.0)^{-2} \quad (17)$$

which is represented by the solid line in figure 4. The estimated standard deviation $s = [\Sigma(\Delta C_p^{\circ}(\text{exp}) - \Delta C_p^{\circ}(\text{calc}))^2 / (n-5)]^{1/2}$ was $4.9 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculated values are shown in table 3.

Table 3. ΔC_p° of ionization of water.

T			T		
$\Delta C_p^{\circ} / \text{J K}^{-1} \text{ mol}^{-1}$			$\Delta C_p^{\circ} / \text{J K}^{-1} \text{ mol}^{-1}$		
K-273.15	exp.	calc.	K-273.15	exp.	calc.
6.00	-287	-284.7	40.00	-193.4	-191.1
10.00	-261.2	-265.3	45.00	-181	-186.0
18.00	-238	-235.3	60.50	-177	-176.8
25.00	-215.2	-216.4	87.50	-177	-178.4
29.00	-208	-207.9	112.50	-189	-189.6
36.00	-195	-196.2	121.25	-199	-194.9
37.50	-200	-194.2	135.00	-202	-204.3

EQUATIONS FOR ΔH_1° AND K_w° AS A FUNCTION OF TEMPERATURE

The equation, for the standard heat capacity change of the ionization of water as a function of temperature, has been used to derive equations to express the temperature dependence of the enthalpy change and the equilibrium constant.

By integration of equation (17) with respect to temperature the following equation was derived to express ΔH_1° as a function of temperature:

$$\Delta H_1^{\circ} / \text{J mol}^{-1} = 2326.4 + 284.964 T - 0.55079 T^2 + 1.7689 \cdot 10^6 (T-197.0)^{-1} \quad (18)$$

where ΔH_1° at 298.15 K has been taken as 55,815 J mol⁻¹ which is the best value as chosen by Olofsson and Hepler. (21)

Integration of equation (18) with respect to temperature leads to the following equation to express $\ln K_w^{\circ}$ as a function of temperature:

$$\ln K_w^{\circ} = -204.520 + 800.18 T^{-1} - 0.066246 T + 28.7918 \ln T + 5.4822 \ln (T-197.0) \quad (19)$$

where pK_w° at 298.15 K has been taken as 13.999. ⁽²¹⁾

RESULTS

The equations (17) - (19) have been used to calculate values of ΔC_p° , ΔH_i° , and pK_w° at rounded temperatures between 273 and 573 K. The results are summarized in table 4.

Table 4. ΔC_p° , ΔH_i° , and $\ln K_w^{\circ}$ of ionization of water.

T	ΔC_p°	ΔH_i°	pK_w°	pK_w°
K - 273.15	J K ⁻¹ mol ⁻¹	kJ mol ⁻¹		Ref. 2
0	- 321.0	62.299	14.944	14.941
25	- 216.4	<u>55.815</u> ^a	<u>13.999</u> ^a	13.993
50	- 182.2	50.918	13.276	13.272
75	- 176.0	46.479	12.710	12.709
100	- 183.1	42.010	12.265	12.264
125	- 197.3	37.266	11.916	11.914
150	- 215.8	32.109	11.646	11.644
175	- 237	26.46	11.444	11.447
200	- 259	20.26	11.299	11.310
225	- 283	13.47	11.205	11.238
250	- 308	6.09	11.156	11.226
275	- 333	-1.93	11.15	11.29
300	- 359	-10.58	11.17	11.43

^a Reference values. ⁽²¹⁾

DISCUSSION

Olofsson and Heppler⁽²¹⁾ have recently reviewed the thermodynamics of ionization of water over wide ranges of temperature and pressure. They used those calorimetrically determined values of ΔH_1° , which they judged as the best available, and derived two different equations to express ΔH_1° as a function of temperature. The equations contained three and five adjustable parameters, respectively. The values of ΔH_1° calculated using their equations agree fairly well with the results from the present work above room temperature. This is of course not surprising, as essentially the same results are used. At lower temperatures, however, the discrepancies become larger, and at 273.15 K our value of $\Delta H_1^{\circ} = 62.299 \text{ kJ mol}^{-1}$ is respectively 0.38 and 0.49 kJ mol^{-1} smaller than the values calculated from their equations. As our equation (18) is based on more recent results, we judge it to give a better description of the temperature dependence of ΔH_1° , than the earlier ones.

The present equation (17) for ΔC_p° as a function of temperature was based on new values of ΔH_1° at ambient temperatures and results from recent flow calorimetric measurements.⁽¹⁴⁻¹⁷⁾ We judge equation (17) to give the best, now available, description of the temperature dependence of ΔC_p° between 273 and 423 K.

Consequently, we think that our equation (19) gives a slightly better description of the temperature dependence of $\ln K_w^{\circ}$ than the corresponding equations in reference 21.

Sweeton, Mesmer, and Baes⁽²⁾ have made an extensive investigation yielding accurate values of pK_w between 273 and 573 K. Their values, recalculated⁽²¹⁾ to refer to the standard-state pressure, are shown in the last column of table 4. The corrections applied to the pK_w values at the saturation pressure in these calculations are small and significant only above 473 K. The values calculated from our equation (19) agree satisfactorily with their values up to 523 K. Considering the experi-

mental difficulties in their measurements, it seems possible that the discrepancies at the highest temperatures may arise from experimental errors.

The results from the present work suggest that an equation of the form as given in equation (16) is useful to express ΔC_p° as a function of temperature. The derived equations for the temperature dependence of ΔH_1° and $\ln K_w^{\circ}$ seem to be well suited for extrapolation purposes.

3. Thermal and volumetric properties of aqueous electrolytes

We have made calorimetric and density measurements on aqueous electrolyte solutions. The results have been used for calculation of apparent molar heat capacities and apparent molar volumes. These apparent molar heat capacities and volumes have been extrapolated to infinite dilution to obtain the corresponding limiting values, which are identical with the desired standard partial molar heat capacities and volumes. Finally, conventional ionic partial molar heat capacities and volumes are calculated.

It is regrettable that there is no international agreement on which symbols to use when expressing apparent molar heat capacities and volumes. Throughout this paper the following symbols will be used:

- $C_{p,\phi}$ for the apparent molar heat capacity of solute,
- V_{ϕ} for the apparent molar volume of solute,
- C_p^{∞} for the apparent molar heat capacity at infinite dilution, which is thermodynamically identical to the standard partial molar heat capacity, $C_{p,2}^{\circ}$, and
- V^{∞} for the apparent molar volume at infinite dilution, which is thermodynamically identical to the standard partial molar volume, V_2° .

EXPERIMENTAL

Our heat capacity measurements have been made with a commercially available flow microcalorimeter, which is designed

by Picker and co-workers at the Université de Sherbrooke and described previously.^(22,23) Our density measurements have been made with a commercially available flow densiometer, based on the oscillating-tube principle, described previously.⁽²⁴⁾ All measurements refer to 298.15 K.

Results of measurements with the Picker flow calorimeter are heat capacities per unit volume of solution. Combination of these heat capacities with the densities that we have also measured and the already known heat capacity of water permits calculation of heat capacities of solution and thence the desired apparent molar heat capacities of solute. Similarly, densities of the solutions lead to the apparent molar volumes of solute.

For both of these calculations we have used the equation

$$Y_{\phi} = [y(\text{soln}) - n_1 y_1^0] / n_2 \quad (22)$$

in which the symbols have the following meanings: Y_{ϕ} is the apparent molar property of solute (heat capacity or volume here), y is the extensive property (heat capacity or volume) of a specified quantity of solution, n_1 is the number of moles of solvent in this specified quantity of solution, y_1^0 is the property (heat capacity or volume) of one mole of pure solvent, and n_2 is the number of moles of solute in the specified quantity of solution. When the solution is one that contains 1000 grams of solvent then n_2 is numerically equal to m , the molal concentration of the solute, and equation (22) can be written for the apparent molar heat capacity as

$$C_{p,\phi} = c_p M_2 + 1000(c_p - c_p^0)/m \quad (23)$$

and for the apparent molar volumes as

$$V_{\phi} = M_2/d + 1000(1/d - 1/d_1^0)/m \quad (24)$$

in which the symbols have the following meanings: $C_{p,\phi}$ is the apparent molar heat capacity of solute expressed in terms of $\text{J K}^{-1} \text{ mol}^{-1}$, c_p and c_p^0 are the heat capacities of solution and of pure water expressed in terms of $\text{J K}^{-1} \text{ g}^{-1}$, M_2 is the

molecular mass of solute in terms of g mol^{-1} , m is the molality of solution expressed in terms of (moles of solute) $(\text{kg H}_2\text{O})^{-1}$, v_ϕ is the apparent molar volume of solute expressed in terms of $\text{cm}^3 \text{mol}^{-1}$, d and d_1^0 are the densities of solution and of water expressed in terms of g cm^{-3} . In all calculations $c_p^0 = 4.1793 \text{ J K}^{-1} \text{ g}^{-1}$ (25) and $d_1^0 = 0.997047 \text{ g cm}^{-3}$ (26) have been used.

Apparent molar properties of strong electrolytes in dilute solutions are accurately represented by the equation

$$Y_\phi = Y^\infty + A_Y (d_1^0 m)^{1/2} + B_Y m \quad (25)$$

in which Y^∞ is the value of Y_ϕ at infinite dilution, A_Y is the limiting slope derived from the Debye-Hückel theory, m is the molality, and B_Y is an adjustable parameter. Our principal interest in this investigation has been to determine the values of C_p^∞ and V^∞ that are identical with the corresponding values of the partial molar properties at infinite dilution.

For the calculations leading to the values of V^∞ we have used the limiting slopes according to Millero. (27)

$$\begin{aligned} A_V (d_1^0)^{1/2} / \text{cm}^3 \text{mol}^{-3/2} \text{kg}^{1/2} &= 1.865 \text{ for 1:1 electrolytes,} \\ &= 9.72 \text{ for 2:1 electrolytes,} \\ &= 27.41 \text{ for 3:1 electrolytes,} \\ &= 58.98 \text{ for 4:1 electrolytes.} \end{aligned}$$

For the calculations leading to values of C_p^∞ we have used the limiting slopes according to Philip and Desnoyers (28) and Leduc, Fortier and Desnoyers. (29)

$$\begin{aligned} A_C (d_1^0)^{1/2} / \text{J K}^{-1} \text{mol}^{-3/2} \text{kg}^{1/2} &= 28.95 \text{ for 1:1 electrolytes,} \\ &= 150.4 \text{ for 2:1 electrolytes,} \\ &= 425.5 \text{ for 3:1 electrolytes,} \\ &= 915.5 \text{ for 4:1 electrolytes.} \end{aligned}$$

Additional calculations have been made for the electrolytes of high charge types, using the limiting slopes for heat capacities according to Silvester and Pitzer. (30)

$$A_C(d_1^0)^{1/2}/J K^{-1} \text{ mol}^{-3/2} \text{ kg}^{1/2} = 523 \text{ for 3:1 electrolytes}$$

$$= 1126 \text{ for 4:1 electrolytes.}$$

COMPARISON OF PICKER FLOW MICROCALORIMETER WITH OTHER CALORIMETERS

Flow microcalorimetry has proven to be very useful for the determination of heat capacities of aqueous electrolyte- and nonelectrolyte solutions. Heat capacities can be determined with high precision, but the accuracy is still uncertain.

Desnoyers and co-workers⁽³¹⁾ have discussed the accuracy of flow microcalorimeters and sources of systematic errors. They defined a correction factor f due to heat leak between the heating element in the calorimeter and the calorimeter jacket. The correction factor f can be calculated from found values of apparent molar heat capacities by the use of the relation:

$$f = (C_{p,\phi} - V_\phi c'_{p,1}) / (C_{p,\phi}^* - V_\phi c'_{p,1}) \quad (26)$$

where $C_{p,\phi}$ is the "true" apparent molar heat capacity, $C_{p,\phi}^*$ is the found apparent molar heat capacity, V_ϕ is the apparent molar volume, and $c'_{p,1}$ is the volumetric heat capacity of water.

These calculated values of f can be used to correct found flow calorimetric results on the dilute solutions.

To calculate the correction factor f according to relation (26) one needs reference values of the apparent molar heat capacity, which can be regarded as "true" values.

To obtain these reference values we made calorimetric measurements on NaCl, KCl, and KNO₃ solutions with one LKB reaction-solution calorimeter, and used the results together with those values of $C_{p,\phi}$ reported in the literature, which we judged as the most reliable. For NaCl solutions good agreement was found between the results reported by Randall and Rossini,⁽³²⁾ by Hess and Gramke,⁽³³⁾ and by Tanner and Lamb⁽³⁴⁾ for molalities

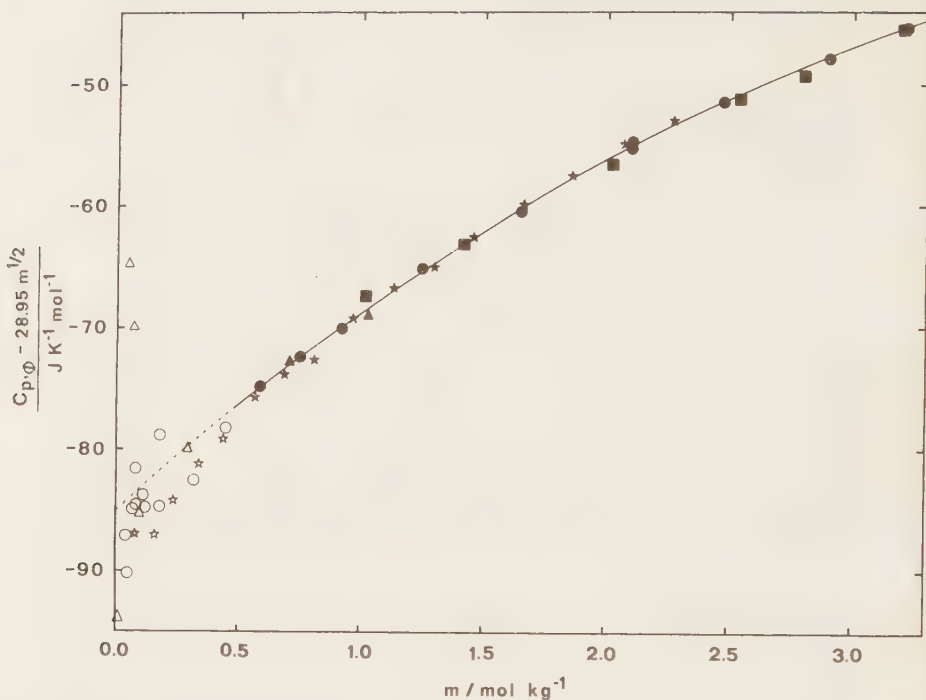


Figure 5. The molality dependence of $C_{p,\phi}$ of aqueous NaCl at 298.15 K. ■ This work, ★ Ref. 32, ▲ Ref. 33, ● Ref. 34.

above 0.5 mol kg^{-1} , as can be seen in figure 5. These values of $C_{p,\phi}$ were used together with our results to derive the following equation to express $C_{p,\phi}$ as a function of molality:

$$C_{p,\phi} / \text{J K}^{-1} \text{ mol}^{-1} = -85.19 + 28.95 m^{1/2} + 18.22 m - 1.827 m^2 \quad (27)$$

which is represented by a solid line in figure 5.

For KCl and KNO_3 the differences between the results from various investigations were larger, and we did not find it meaningful to derive any equations to express $C_{p,\phi}$ as a function of temperature.

To calculate the values of the correction factor f , for our two flow microcalorimeters (1 and 2), measurements were made on concentrated solutions (0.5 to 3.0 mol kg⁻¹) of NaCl, KCl, and KNO₃. Similar measurements on NaCl and KCl solutions have been reported in the literature.^(22,35) We have used the results from all these measurements to calculate the value of the correction factor f , for each calorimeter.

These calculated f values have been used to correct the values of $C_{p,\phi}$ of the electrolytes in dilute solutions (0.05 to 0.50 mol kg⁻¹), determined with the same calorimeters.

C_p^∞ OF AQUEOUS NaCl, KCl, AND KNO₃

The corrected values of $C_{p,\phi}$ were fitted by a least squares method to equation (25) with the limiting slope specified above. The results are summarized in table 5. Other results from flow microcalorimetric measurements reported in the literature^(14,16,17) are shown there as well. The values of the correction factor f , which have been used to correct the apparent molar heat capacities are listed in the second column.

Heat capacity measurements on aqueous NaCl seem to be very reproducible and we support the recommendation by Desnoyers et al.⁽³¹⁾ for NaCl to be used as a chemical standard in flow calorimetric measurements on aqueous electrolyte solutions. As the best value of the partial molar heat capacity of aqueous NaCl we chose the average of the values shown in table 5 $C_p^\infty = -84.3 \text{ J K}^{-1} \text{ mol}^{-1}$.

ACCURACY OF PICKER FLOW MICROCALORIMETER

The accuracy of Picker flow microcalorimeter is estimated as indicated from the present study.

When we correct our results from flow microcalorimetric measurements using the correction factor f , defined by Desnoyers et al.⁽³¹⁾ we get very good agreement between

Table 5. Parameters for equation $C_{p,\phi} = C_p^\infty + A_C (\bar{d}_1^0 m)^{1/2} + B_C m$

Investigator	f	$\frac{C_p^\infty}{J K^{-1} mol^{-1}}$	s_e	$\frac{B_C}{J K^{-1} mol^{-2} kg}$	s_B
NaCl					
Present study ^a	1.020	-84.5	0.3	15.3	0.6
Present study ^b	1.043	-83.8	0.4	16.0	1.3
Present study ^c	1.012	-85.4	0.7	14.8	1.6
Present study ^d	1.021	-83.5	0.6	12.3	1.7
Reference 14	1.020	-84.6	0.4	13.4	1.3
Reference 17	1.000	-84.1	0.3	15.9	1.3
KCl					
Present study ^a	1.013	-116.1	0.7	7.2	1.8
Present study ^d	1.027	-115.8	1.0	7.0	2.5
Reference 14	1.020	-114.1	0.2	6.7	0.7
KNO ₃					
Present study ^b	1.030	-59.4	0.5	51.9	1.8
Reference 16	1.000	-59.8	0.4	49.9	1.7

^aCalorimeter 1, ^bCalorimeter 2, ^cFrom reference 22,
^dFrom reference 35.

the results from measurements made with different calorimeters (see table 5). But there are some problems as there are indications that the correction factor f can vary from one calorimeter to another, and seems to be slightly dependent on the electrolyte. Further investigations are needed to make clear how to best indicate and correct for these small systematic errors in flow microcalorimeters. This investigation indicates an unacceptable large systematic error for the

calorimeter 2. The source of this error should be detected and corrected before the calorimeter is used in other studies. For the calorimeter 1 this investigation leads to corrections in the partial molar heat capacities of -3.0 and $-2.9 \text{ J K}^{-1} \text{ mol}^{-1}$ for NaCl and KCl, respectively. Even though these corrections are larger than expected, they are within the uncertainty limits $\pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$ earlier claimed for this calorimeter. However, even if we do not know how to best correct for these small systematic errors, the results from flow microcalorimetric measurements are superior in accuracy compared to the results from most previous measurements.

C_p^∞ AND V^∞ OF AQUEOUS ELECTROLYTES OF CHARGE TYPES 1:1 AND 2:1

The results from our calorimetric and density measurements on solutions, at 8 to 10 different molalities, have led to apparent molar heat capacities, $C_{p,\phi}$ and apparent molar volumes, V_ϕ , of solute, according to the relations (23) and (24). These values of $C_{p,\phi}$ and V_ϕ have been fitted by a least squares method to equation (25). The found values of the properties at infinite dilution and the B parameters are summarized in table 6.

We are unable to make any direct comparisons of our C_p^∞ values for these electrolytes with earlier results. We can, however, make some indirect comparisons. They are most conveniently made in terms of conventional ionic heat capacities based on $C_p^\infty (\text{H}^+) = 0$.

$C_p^\infty (\text{M}^{2+})$ OF EIGHT AQUEOUS CATIONS

We have calculated the conventional ($C_p^\infty (\text{H}^+) = 0$) ionic partial molar heat capacities for the eight $\text{M}^{2+}(\text{aq})$ cations that we have investigated. We have used: $C_p^\infty (\text{ClO}_4^-) = -26 \text{ J K}^{-1} \text{ mol}^{-1}$ from earlier investigations of various perchlorates of univalent cations, $C_p^\infty (\text{NO}_3^-) = -72 \text{ J K}^{-1} \text{ mol}^{-1}$ from nitrates of univalent cations, $C_p^\infty (\text{Cl}) = -127$

Table 6. Parameters for equation (25).

Solute	C_p^∞	B_c	V^∞	B_V
	$J K^{-1} mol^{-1}$	$J K^{-1} mol^{-2} kg$	$cm^3 mol^{-1}$	$cm^3 mol^{-2} kg$

Paper V				
$Ca(ClO_4)_2$	-76.8	-55.6	70.8	-2.1
$Cd(ClO_4)_2$	-57.4	-117.1	73.8	-11.2
$Co(ClO_4)_2$	-81.0	-100.7	62.8	-12.0
$Mn(ClO_4)_2$	-61.7	-139.0	70.8	-10.2
$Ni(ClO_4)_2$	-93.1	-109.7	59.8	-11.1
$Zn(ClO_4)_2$	-73.1	-80.9	63.5	-9.9

Paper VI				
$Ca(NO_3)_2$	-170.0	11.4	39.4	-7.2
$Co(NO_3)_2$	-170.2	-75.9	33.4	-8.3
$Cu(NO_3)_2$	-161.2	-81.3	33.6	-15.2
$Mg(NO_3)_2$	-160.1	-68.5	36.9	-8.0
$Mn(NO_3)_2$	-156.0	-56.5	40.7	-4.2
$Ni(NO_3)_2$	-186.5	-87.8	29.7	-10.9
$Zn(NO_3)_2$	-165.3	-50.0	33.6	-9.1

Paper VII				
Na_2SO_4	-190.1	133.0	11.4	0.8
K_2SO_4	-251.0	73.6	32.8	2.4
$Na_2S_2O_3$	-163.6	106.0	26.3	3.0
$Na_2S_2O_8$	-29.3	50.9	76.1	-2.4
$K_2S_2O_8$	-84.0	160.0	97.6	-6.9
K_2CrO_4	-235.0	36.6	38.2	0.2
Na_2MoO_4	-122.8	31.1	28.0	-0.5
Na_2WO_4	-110.4	7.8	30.0	-2.8

Paper VIII				
$NaIO_3$	-29.6	148.0	24.8	2.7
$KMnO_4$	1.5	69.2	51.6	-1.3
$MnCl_2$	-259.3	-52.2	18.3	-8.6

$\text{J K}^{-1} \text{mol}^{-1}$ from chlorides of univalent cations.⁽³¹⁾ The results are shown in table 7. Earlier reported values^(31,37) are included in the table.

Table 7. Conventional ($C_p^\infty (\text{H}^+) = 0$) ionic heat capacities at 298.15 K.

Ion	$C_p^\infty / \text{J K}^{-1} \text{mol}^{-1}$		
	M (NO_3) ₂	M (ClO_4) ₂	M Cl_2
Ca^{2+}	- 26	- 25	- 28 ^{a,b}
Cd^{2+}	- 8 ^b	- 5	
Co^{2+}	- 26	- 29	- 25 ^b
Cu^{2+}	- 17	- 18 ^b	
Mg^{2+}	- 16	- 12 ^b	- 15 ^a
Mn^{2+}	- 12	- 10	
Ni^{2+}	- 42	- 41	- 40 ^b
Zn^{2+}	- 21	- 21	

^a Reference 31, ^b Reference 37.

As can be seen from table 7, the agreement is good between the values of $C_p^\infty (\text{M}^{2+})$ calculated from the results of measurements on different electrolytes. The discrepancy is only a few $\text{J K}^{-1} \text{mol}^{-1}$ and it is at most $4 \text{ J K}^{-1} \text{mol}^{-1}$.

$C_p^\infty (\text{X}^-)$, $C_p^\infty (\text{M}^+)$, AND $C_p^\infty (\text{M}^{2+})$ VERSUS THE IONIC RADIUS

The values of the partial molar heat capacities of the aqueous cations in table 7 are plotted versus the crystal ionic radius in figure 6, together with some values of univalent and divalent ions which have been reported in the literature.⁽³¹⁾

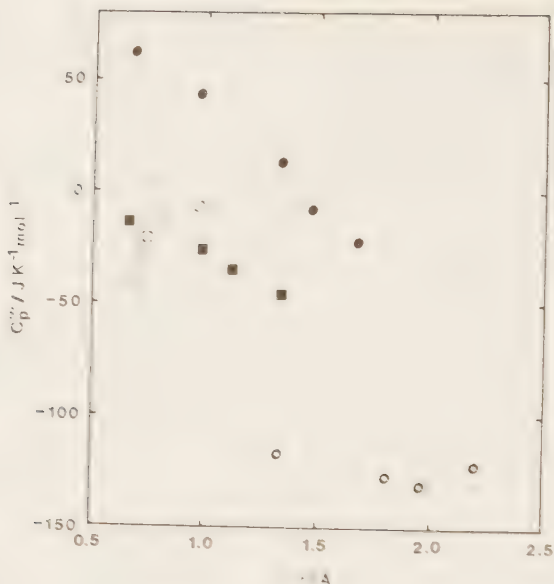


Figure 6. The ionic partial molar heat capacities versus the ionic radius.

★ F^- , Cl^- , Br^- , I^- , ● Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , ■ Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , □ Ni^{2+} , Co^{2+} , Cu^{2+} , Mn^{2+} , ○ Zn^{2+} , Cd^{2+}

The partial molar heat capacities of the ions, from the groups 1a, 2a, and 7a in the Periodic table, appears to vary regularly within each group. It seems reasonable to assume that some of this regularity will be kept at other temperatures, which would be appreciated in further investigations.

C_p^∞ AND V^∞ OF AQUEOUS $Cr(NO_3)_3$, $LaCl_3$, $K_3Fe(CN)_6$, AND $K_4Fe(CN)_6$

The results from our calorimetric and density measurements have led to apparent molar heat capacities, $C_{p,\phi}$, and apparent molar volumes, V_ϕ , of solute, according to relations (23) and (24). These $C_{p,\phi}$ and V_ϕ have been fitted by a least squares method to equation (25) with the limiting slopes $C_{p,\phi}^\infty$ and V_ϕ^∞ defined above. The results are summarized in tables 1 and 2.

Table 8. Volumetric parameters for equation (25)

Solute	V^{∞}	B_V
	$\text{cm}^3 \text{ mol}^{-1}$	$\text{cm}^3 \text{ mol}^{-2} \text{ kg}$
$\text{Cr}(\text{NO}_3)_3$	45.4	-41.1
$\text{LaCl}_3 \text{ (m} < 0.04\text{)}$	14.3	-54.9
$\text{K}_3\text{Fe}(\text{CN})_6$	146.6	-24.6
$\text{K}_4\text{Fe}(\text{CN})_6$	113.3	-43.4

Table 9. Heat capacity parameters for equation (25)

Solute	Desnoyers' limiting slope		Pitzer's limiting slope	
	C_p^{∞}	B_c	C_p^{∞}	B_c
	$\text{J K}^{-1} \text{ mol}^{-1}$	$\text{J K}^{-1} \text{ mol}^{-2} \text{ kg}$	$\text{J K}^{-1} \text{ mol}^{-1}$	$\text{J K}^{-1} \text{ mol}^{-2} \text{ kg}$
$\text{Cr}(\text{NO}_3)_3$				
m < 0.04	-223	-2337	-231	-2644
m < 0.06	-242	-1628	-251	-1887
LaCl_3				
m < 0.04	-456	-898	-464	-1203
m < 0.09	-465	-580	-475	-805
$\text{K}_3\text{Fe}(\text{CN})_6$	-206.5	-300	-218.7	-478
$\text{K}_4\text{Fe}(\text{CN})_6$	-460	-688	-481	-1141

We have calculated C_p^{∞} of aqueous $\text{Cr}(\text{NO}_3)_3$ and LaCl_3 using apparent molar heat capacities covering different ranges of molality. Depending on which molality range is used, values of C_p^{∞} differ by about $20 \text{ J K}^{-1} \text{ mol}^{-1}$ for $\text{Cr}(\text{NO}_3)_3$ and around

$10 \text{ J K}^{-1} \text{ mol}^{-1}$ for LaCl_3 . Depending on which value of the limiting slope is used, the values of C_p^∞ differ by about $10 \text{ J K}^{-1} \text{ mol}^{-1}$ for the 3:1 electrolytes and $21 \text{ J K}^{-1} \text{ mol}^{-1}$ for the 4:1 electrolyte $\text{K}_4\text{Fe}(\text{CN})_6$.

We have not been able to use results from other investigations to help us to choose between the various C_p^∞ values listed in table 9. In spite of the uncertainties in our measurements and those from our calculations based on the different limiting slopes, we believe that our C_p^∞ values in table 9 are the best ones, now available, for aqueous electrolytes of 3:1 and 4:1 charge types.

THE LIMITING SLOPE DERIVED FROM THE DEBYE-HÜCKEL THEORY

In connection with our investigations of heat capacities of aqueous electrolytes, of charge types 1:1 and 2:1, we have used $A_C(d_1^0)^{1/2} = 28.95$ and $150.4 \text{ J K}^{-1} \text{ mol}^{-3/2} \text{ kg}^{1/2}$, respectively. These values are based on earlier analyses, ^(28,29) and have been used in connection with many similar investigations at the Université de Sherbrooke and elsewhere. Calculations by Spitzer ⁽³⁸⁾ and by Silvester and Pitzer ⁽³⁰⁾ have led to values of $A_C(d_1^0)^{1/2}$ about 10% and about 25% larger, respectively, than these values quoted above. Application of equation (25) to typical values of $C_{p,\phi}$ of 1:1 electrolytes at 298.15 K is not critically dependent on whether we use Desnoyers' ^(28,29) or Pitzer's ⁽³⁰⁾ values for the limiting slope, because derived values of C_p^∞ differ by only about $1 \text{ J K}^{-1} \text{ mol}^{-1}$. This is about one-third of the commonly estimated uncertainty associated with heat capacities obtained recently in both Sherbrooke and Lethbridge. Similar application of equation (25) to values of $C_{p,\phi}$ of 2:1 electrolytes, shows that the C_p^∞ values derived on the basis of the two different slopes under present consideration differ by about $6 \text{ J K}^{-1} \text{ mol}^{-1}$ which is a little larger than previously estimated uncertainties in these values.

If it were possible to make heat capacity measurements of sufficient accuracy on very dilute solutions, it would then be possible to derive accurate C_p^∞ values and also limiting slopes by plotting C_p^∞ versus $m^{1/2}$. Since this simple approach is made unsatisfactory by our inability to make sufficiently accurate heat capacity measurements on sufficient dilute solutions, we are forced to make use of some approach based on an equation like (25). Application of equation (25) with three adjustable parameters (C_p^∞ , A_C , and B_C) to presently available heat capacities is generally unsatisfactory because it is possible to fit the experimental results, with a range of values of the three parameters, that is unacceptable large. We note, however, that modest improvements in our ability to measure heat capacities of dilute solutions may suffice to make one of the approaches described here useful in the future. Our best presently available approach to analysis of heat capacities of dilute solutions is based on equation (25) with the limiting slopes derived from the Debye-Hückel theory and the properties (density and dielectric constant) of water.

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